

CHEMISTRY OF
DYE STUFFS

G. VON GEORGIEVICS

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CHEMISTRY OF DYE-STUFFS

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BY

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TRANSLATED FROM THE SECOND GERMAN EDITION BY

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LONDON

SCOTT, GREENWOOD & SON

"THE OIL AND COLOUR TRADES JOURNAL" OFFICES

8 BROADWAY, LUDGATE HILL, E.C.

CANADA: THE COPP CLARK CO., LTD., TORONTO
UNITED STATES: D. VAN NOSTRAND CO., NEW YORK

1903

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P R E F A C E.

ORIGINALLY designed to form a section of a textbook on the Technology of the Textile Fibres, the present work was afterwards modified into a separate volume, chiefly in order to render it more accessible to chemists interested in the chemistry of dye-stuffs rather than in the dyeing and cloth printing industries. This change led to a more exhaustive treatment of the dye-stuffs, and the omission of all particulars relating to their practical application, the latter being relegated to the companion volume* dealing also with the improvement of the fibres by bleaching, etc. Only in the sections treating of natural dye-stuffs and mineral colours has more attention been paid to the technical side, because the present volume is primarily designed for the dyer's chemist.

The aim in view was to provide a textbook presenting to the student in as lucid and condensed a form as possible the extremely wide domain of the modern chemistry of dye-stuffs.

* *Chemical Technology of Textile Fibres.* Scott, Greenwood & Co., 1902. 10s. 6d. net.

Care has been taken to bring into prominence all the relations known to subsist between the various dyes and groups of dyes, as well as the connection between colour and constitution, since the proper appreciation of these relations forms the main object of colour chemistry.

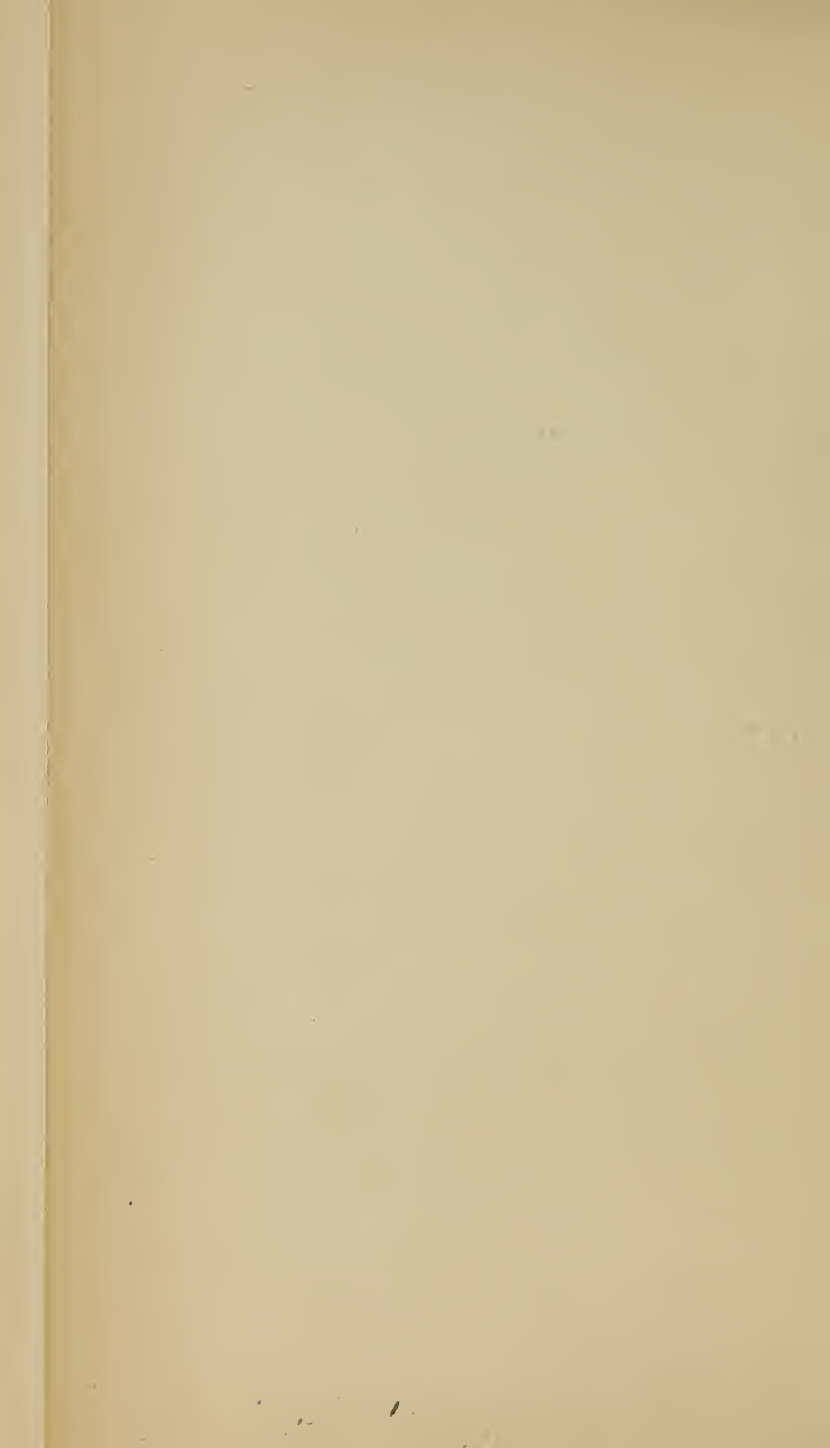
In order to present to the student an accurate picture of the modern aspect of this branch of chemistry, an endeavour has also been made to clearly define the true importance attaching to the several dye-stuffs, whether theoretically, practically, or historically. The student is merely assumed to have some knowledge of the most important facts in organic chemistry—more especially as concerns the aromatic compounds.

Owing to the progress made in connection with dye-stuffs since the appearance of the first edition, the sections dealing with the azo dye-stuffs, triphenylmethane dye-stuffs, phthaleins and azines have been considerably modified, and those treating of the flavones and the sulphur dyes are entirely new. In both editions great assistance in going through the MS. has been rendered by Dr. C. Duisberg, of Elberfeld, whose aid is gratefully acknowledged.

GEORGIEVICS.

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INTRODUCTION.*

CLASSIFICATION AND GENERAL PROPERTIES OF DYE-STUFFS.

UP to the middle of the last century the only dyes available for the decoration of fabrics by dyeing and printing belonged to the vegetable kingdom, together with the colouring matters of a few insects and snails and sundry mineral pigments. The few artificial dye-stuffs already known, such as picric acid and rosolic acid, were not at that time used in dyeing.

In 1856 Mauveine was discovered by Perkin, and in 1859 a far more important dye-stuff, Fuchsine, was discovered by Verguin, thus laying the foundation of the present important industry of the artificial dye-stuffs, generally known as coal-tar dyes, and of which over a thousand are now in use.

At the outset a distinction was drawn between these and natural dye-stuffs, the chief reason for this being due to the properties of the artificial dye-stuffs first produced. These were mainly much handsomer and brighter, but not so fast as the majority of the natural dyes, and by a somewhat hasty generalisation, artificial dyes were at first regarded as handsome but fugitive—a prejudice which for a long time acted adversely on the artificial dyes, and which was only removed on the introduction of the Alizarine dyes

* The historical development of the tar colour industry is given at the end.

in the seventies. This prejudice was also probably supported by the opinion then prevailing that natural substances resulting from the vital activity of animals and plants could not be prepared by artificial means.*

At the present time we have artificial dyes some of which are just as fast as, and others even more so than, those of natural origin; and moreover the problem of the artificial preparation of natural dyes is now partly solved (Alizarine, Indigotine).

It is now known that no distinctive difference separates the two classes artificial and natural, and that they are almost without exception derivatives of benzol, and therefore aromatic compounds. Nevertheless the old classification into "natural" and "artificial" dyes may still be retained until the constitution of the former has been definitely settled. As a further means of distinction, attempts have been made to classify dyes in accordance with their behaviour in the dyeing of fabrics; thus Bancroft distinguished between substantive and adjective dyes. He gave the name of substantive to all dyes capable in themselves of dyeing fabrics; whereas adjective dyes are those requiring the assistance of a mordant.†

However, we are now acquainted with dyes that act "direct," *i.e.*, are capable of dyeing either alone or of being fixed by the aid of a mordant; also with others which can neither be used for direct dyeing nor yet with the aid of a mordant. To these belong Indigo and Aniline Black, which therefore cannot be classified at all under this system.

Hummel divides dyes into "monogenetic" and "polygenetic," the former class, *e.g.*, Fuchsine, being only able to

* Wohler's synthesis of urea was, however, effected as long ago as 1828.

† Certain metallic salts. Other substances, such as tannin, which are also occasionally termed mordants, will be referred to in the following pages as fixing agents.

produce one colour (in various shades), whereas the poly-genetic dyes, *e.g.*, Alizarine, can produce different colours according to the mordant employed. The former class corresponds to the substantive; the latter to the adjective dyes. This classification, however, suffers from the same defects as that of Bancroft.

Von Perger distinguishes between dyes and dye-stuffs according as they are in themselves sufficiently strong to produce the effect of dyeing, or can only be regarded as fundamental dyeing materials, which, when used alone, are, by reason of insufficient tinctorial power, incapable of producing a useful result, and have therefore to be converted into dyes by combination with a mordant. Consequently, Fuchsin is a dye, Aniline a dye-stuff.

The dye-stuffs, therefore, inevitably require the assistance of a mordant, whereas the dyes are themselves capable of dyeing without a mordant, and only occasionally need the assistance of a mordant or fixing agent to insure the better fixing and developing of the colour. This classification has the great advantage of distinguishing between the substantive dye-stuffs and the mordant dye-stuffs, which are fundamentally different from each other.

The individual terms, substantive, adjective, monogenetic and polygenetic dyes and dye-stuffs, can be very properly used for characterising the dyeing properties of dye-stuffs; but as a means of classification in general, these distinctions are unsuitable.

From the practical standpoint the only true principle of classification is the method of using the dye-stuffs. Such a simple classification, however, as has hitherto been attempted is impossible, owing to the highly divergent nature and methods of using dyes.

In the following lines the dye-stuffs are divided into eight classes.

1. **Acid Dye-stuffs.**—Mostly sodium salts of sulpho or carbon acids or nitro compounds. To this series belong picric acid, most of the azo dyes, Eosine, etc. These dye wool and silk direct in an acid bath, *i.e.*, are used in conjunction with an acid or an acid salt. They are not well adapted for dyeing cotton.

2. **Tannin Dye-stuffs.**—Mostly salts of colour bases with hydrochloric acid. They are sometimes, though not very correctly, termed basic dyes; they dye wool and silk direct without any addition; cotton with the aid of tannin. To this class belong Fuchsine, Auramine, etc.

3. **Dye Salts.**—So called because they are used in conjunction with neutral or alkaline salts. The term substantive cotton dyes, frequently applied to these, is not altogether appropriate, some of them being also very good dyes for wool. These dyes are generally sodium salts of sulpho or carbon acids, which are also absorbed by the fibre as such. They are capable of dyeing cotton direct, with certain additions to the dye bath, such as common salt, Glauber salt, etc., and are fixed on wool and silk in a similar manner.

The class embraces Benzidine dyes, Primuline dyes, etc.

4. **Sulphur Dyes.**—A new class producing washing fast colours on cotton in an alkaline bath; generally, with addition of soluble sulphides, the development of the true dye, however, being usually effected by oxidation subsequent to absorption by the fibre. They consequently occupy a new position leading to the next class of

5. **Vat Dyes**, which, by reason of their inert chemical character, have no affinity for textile fibres, and can only be fixed thereon by reduction or subsequent oxidation. To these belong Indigo and Indophenol Blue.

6. **Mordant Dyes** are all of an acid character, and can only be fixed on the fibre by the aid of mordants. The Alizarine dyes, wood dyes, etc., belong to the class.

7. **Developing Dyes.**—These include such dye-stuffs as, being insoluble, cannot be used for dyeing, and must therefore be first produced upon the fibre, *e.g.*, p. Nitraniline Red (an azo dye), Aniline Black, etc.

8. **Albumin Dyes** cannot be employed by any of the foregoing methods, since they require to be fixed on the fibre by an agglutinant, for which purpose albumin is most suitable. They include the colour lakes and the majority of mineral pigments.

This method of classification greatly facilitates the study and review of the practical application of the dye-stuffs, and is derived from practical experience, as described in the Author's *Chemical Technology of Textile Fibres*.

In the present volume, which deals theoretically with dyes, the constitution of the latter is the sole criterion of classification. The old subdivision into aniline, phenol, naphthol, etc., dyes does not fulfil these requirements, entailing as it does the grouping together of dye-stuffs of sometimes very divergent constitution.

At the present time dye-stuffs are classified after the generally accepted proposition of O. N. Witt, namely, in accordance with the groups from which their character as dye-stuffs is derived. Witt calls these "chromophorous" groups. They form, in the first place, the so-called "chromogens," or fundamental substances of dye-stuffs, which are only converted into true dyes by a change effected in their inert chemical character by the introduction of salt-forming substances.

Example: — $\text{N} = \text{N}$ — is a chromophorous group; azobenzol, $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_5$, is, it is true, red in colour, but is not a dye. If, however, its inert chemical character be modified by the introduction of salt-forming substances, dye-stuffs are produced. $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_4\text{NH}_2$ (amidoazobenzol) and $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_4\text{OH}$ (oxyazobenzol) are dyes.

Azobenzol is therefore a chromogen. Speaking generally, it may be said that only such organic compounds are dye-stuffs as contain acid or basic groups, or both together; consequently an organic substance that contains, for example, merely phenyl and methyl groups is not a dye-stuff. In this respect by far the most important part is played by the hydroxyl and amido groups; their share in the formation of the dye and the characteristics of the dye-stuffs is so great that one is compelled to assume the existence of a reaction (for the most part still undetermined) between them and the chromophorous groups. In the case of the nitroso dye-stuffs a relation of this kind is now expressed in their structural formulæ. In the chromophorous NO_2 and CO groups, which of themselves are unable to produce dye-stuffs, the acidifying influence they exert upon the OH groups present is just as remarkable as the development of tinctorial character ensuing on the introduction of hydroxyl groups into such aromatic substances as contain the aforesaid chromophorous groups. On this account the name of auxochromes has been applied to the OH and NH_2 groups.

A very important part is also played by the SO_3H group in the chemistry of organic dye-stuffs. Its influence is manifested, in the first place, by imparting an acid character to the molecule of the dye-stuff into which it enters, the latter being converted into an acid dye. Furthermore, if previously insoluble in water, the dye is now rendered soluble, a condition frequently precedent to the possibility of its practical application in dyeing. The sulpho group, however, is not an auxochrome, and, in fact, its introduction into a dye-stuff rather weakens the tinctorial power of same. Sometimes the position occupied by this group in the molecule of the dye-stuff is of only slight influence on the colour and dyeing properties, though mostly the influence is very considerable. So far as one is justified in drawing conclusions in this

respect from the properties of a few azo dye-stuffs, it may be said that the influence of the sulpho group upon the dye is the greater in proportion as it is nearer to the chromophorous group.

According to Geigy, the trialkylammonium group has the property of rendering insoluble azo dyes soluble.

It is only of late that chlorine has attained a position of any importance as a substituent for dye-stuffs. It has been found that triphenylmethane dye-stuffs are converted into acid dye-stuffs by the introduction of chlorine, and that the products are faster and of bluer tinge than the originals.

The carboxyl group has only a slight influence on the shade of a dye-stuff; on the other hand, it increases the fastness of the dyeing, and for the most part enables the dye-stuff to form "lakes" with mordants.

Finally, the alkyls do not exert any special influence on the character of a dye-stuff when introduced into the molecule. Alkyl-oxy groups, on the other hand, render a dye-stuff considerably bluer, and improve its beauty and tinctorial power.

As an instance of this, the dyeings obtained with Azo Blue may be compared with those from Benzazurine; those of the Ponceau dyes with those of Coccinine; and Azococcine with Azoeosine. Generally speaking, it may be said that by continuing to introduce groups into the molecule of a dye-stuff, the colour of same can be changed from yellow to red, Bordeaux, and blue, this being particularly noticeable in the case of many simple azo dyes. Consequently the simplest dye-stuffs are greenish-yellow or yellow; but, as the molecular weight increases, the colour changes to orange red, violet and blue, in succession.

This law was discovered quite empirically by Nietzki, and scientifically confirmed through the investigation of

the absorption spectra of a series of dye-stuffs by Schütze.* Although our information is fairly good with regard to the influence exerted by various substances on the character of a dye-stuff, we still know very little as to the cause of the dyeing power of any of these compounds, or of the connection between the constitution of a body and its colour. In other words, the term "chromophorous group" is very ill-defined, and is really nothing more than a name employed to indicate an atomic condition common to a number of dye-stuffs. The coloration of an organic substance does not depend solely on the chromophore, but must be regarded as the total effect of several factors.

In many instances a chromophorous group alone is incapable of producing a chromogen; thus, for example, the mononitrophenols are not dye-stuffs, and only become such on the introduction of several nitro groups. In general it may be said that a chromophorous group will produce the expected coloration effect the more readily in proportion as the atomic complex into which it is introduced is richer in carbon. When a chromophore is introduced into a compound that is already a dye-stuff it deepens the colour. In the case of the azo dye-stuffs especially, it has been observed that the tinctorial power is so much the greater the wider the interval between the introduced azo group and that already present. Formerly it was believed that only organic compounds containing nitrogen, oxygen, or sulphur could exhibit colour, and it was laid down as a rule that hydrocarbons must be colourless. This rule, however, has been proved untenable by the discovery of several coloured hydrocarbons. Probably the most instructive instance of this kind is that recently communicated by Thiele.† He

* *Zeitschr. f. Phys. Chem.* (1892), 9, 109.

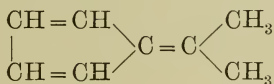
† *Berl. Ber.*, 1900, pp. 666-673.

found that cyclopentane, $\begin{array}{c} \text{CH} = \text{CH} \\ | \\ \text{CH} = \text{CH} \end{array} \rangle \text{CH}_2$, is endowed with

a motility of the methylene hydrogen (hydrogen of the CH_2 group) not otherwise met with in hydrocarbons but only in ketones. This hydrocarbon reacts with diazo compounds, thus differing from other hydrocarbons. It also gives, with aldehydes and ketones, orange to blood red hydrocarbons, which are derivable from the hypothetic (not yet prepared) "fulvene," which is the name applied by

Thiele to the hydrocarbon $\begin{array}{c} \text{CH} = \text{CH} \\ | \\ \text{CH} = \text{CH} \end{array} \rangle \text{C} = \text{CH}_2$. With acetone,

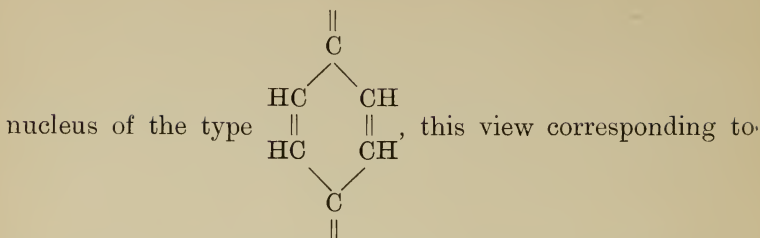
for example, the compound



is produced. The existence of the fulvenes shows, in the first place, that coloured organic compounds are not necessarily of such complex composition as was hitherto believed. From this fact we must also draw the vitally important conclusion, so far as the chemistry of colours is concerned, that the coloration of organic compounds is greatly influenced by the method of arrangement of the double compounds.

Even before the discovery of the fulvenes, it was pretty generally assumed that double combinations are a chief cause of colour in organic compounds, the main reason for this view being the ease with which the organic dyes can be reduced (dissociation of the double compound) to colourless, so-called "leuco-compounds," which, in turn, can for the most part be readily reconverted into the original dye-stuffs by oxidation.

Latterly the majority of dye-stuffs have been regarded as bodies of the quinone class, but derived from a benzol

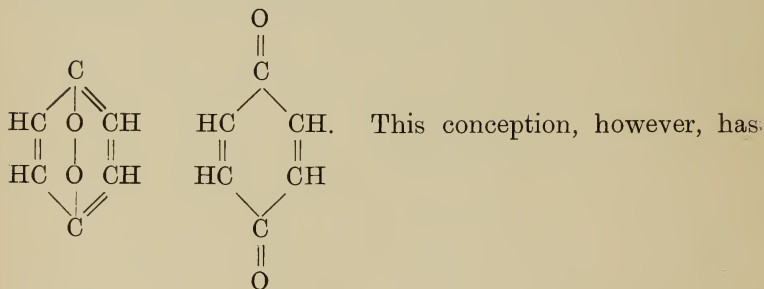


the more recent conception of the quinones as diketones :

QUINONE.

Old formula.

New formula.



not yet received general acceptance. According to Armstrong, *all* coloured organic compounds have a structure like quinone; but this hypothesis is contradicted by azobenzol, for example, to which the formula ($\text{C}_6\text{H}_5\text{N}=\text{N}-\text{C}_6\text{H}_5$) is still held to apply.

A very interesting series of facts, apparently having some reference to the question of the origin of coloration, have recently been discovered by Hugo Kaufmann.* He assumes that in different benzol derivatives the benzol ring occurs in divergent conditions, which may be distinguished by the exhibition of well-defined properties. When the vapours of aromatic compounds are subjected to Tesla currents, a number of them become luminous even at atmospheric pressure, whereas ordinarily the energy of the current is transformed into light only, when the vapours are in a greatly

* *Berl. Ber.*, 1900, p. 1725.

diluted condition. This worker has established the existence of a highly interesting relation; he finds that the property of becoming luminous is possessed by the vapours of such benzol derivatives as have a tendency to pass into a quinone-like state of linking in the benzol ring. This condition he terms the "*x*-condition". Bodies of this class are also in general more easily oxidised. Benzol itself is nearly non-luminous, whilst naphthalene and other hydrocarbons having several directly connected benzol nuclei are luminous. The luminosity is also greater in the case of para compounds than with ortho and meta derivatives. Acetylene groups and negative groups (NO_2 in particular) exert an opposing influence, and also diminish the facility of oxidation. Coloured benzol derivatives are non-luminous; leuco compounds of dye-stuffs (so far as these have been investigated) are luminous, *e.g.*, leuco-malachite green.

COMBINATION OF DYE-STUFFS WITH MORDANTS.

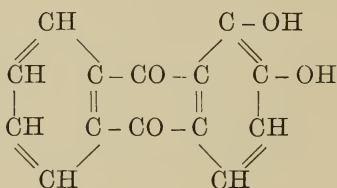
By the name "mordants" is understood various metallic salts, the oxides of which form, with dye-stuffs, insoluble and very stable coloured compounds, known as "lakes". The nature of the latter still remains uninvestigated, but they are regarded as salts, a view, however, that is at variance with their resistance to decomposition by acids.

The compounds of alizarine with potash, soda, lime, etc., are decomposed by acetic acid in the cold; on the other hand, the alizarates of iron, chromium, alumina and tin are only split up by prolonged boiling with dilute mineral acids, and therefore these compounds alone are lakes, the others being of the nature of salts.

Notwithstanding the large accumulation of facts at disposal, the connection between the constitution of a dye-stuff and its ability to form lakes with mordants has only been

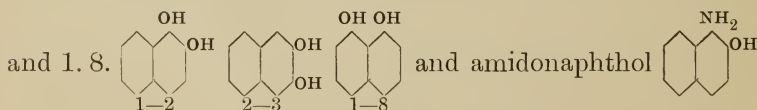
partly established. The possession of this capacity is attributed to the OH and COOH groups; the strongly acid SO_3H group is not only incapable of forming lakes, but, moreover, its introduction into the molecule of a mordant dye-stuff reduces the lake-forming power of the latter—its position in the molecule, however, has considerable influence in this respect. This fact affords additional evidence against the view that the colour lakes are compounds of the nature of salts. The nitro group also behaves in a similar manner.

The clearest insight into the relation between the constitution and lake-forming properties of the alizarine and nitroso dye-stuffs has been afforded by the researches of Graebe, Liebermann and Kostanecki. Alizarine contains two OH groups in a relative ortho position, and one of them is adjacent to a CO group, in accordance with the formula :



It may be laid down as a rule that only such anthraquinone derivatives are mordant dye-stuffs as contain two OH groups in the same (1. 2.) position as alizarine; hence monoxanthraquinone, dioxanthraquinone (containing one hydroxyl in each nucleus), and 2. 3. dioxanthraquinone, are not mordant dye-stuffs.

Similar instances of uniformity also occur in the naphthalene series, inasmuch as the dioxynaphthalenes 1—2, 2. 3.

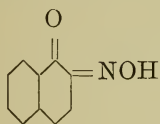


furnish mordant azo dye-stuffs when combined with a diazotised amine.

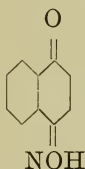
Salicylic acid also produces mordant dye-stuffs when it occurs as a component of azo bodies. The latter, however, are not so stable as the first named.

This "Liebermann and Kostanecki's law" applies solely to such anthraquinone derivatives as contain only OH groups; if other groups (*e.g.*, amido groups) be present, the capacity for forming lakes may also exist without the OH groups being in the ortho position. In the case of other groups of dye-stuffs, *e.g.*, the xanthenes (*q.v.*), the above law is inoperative.

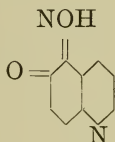
With the nitroso dye-stuffs, which are all nitrosophenols, Kostanecki found the law to prevail that they dye mordants only when the substituent groups are present in the ortho position, *e.g.* :—



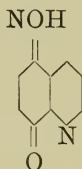
Dyes mordants.



Does not dye mordants.



Dyes mordants.



Does not dye mordants.

The last of these examples is also noteworthy, inasmuch as, according to Noeltig, orthoquinophenol



colours mordants, whilst the corresponding para derivative does not. Consequently the introduction of the nitroso group confers the aforesaid property on p. quinophenol, whereas the mordant dyeing o. quinophenol is thereby deprived of its power.

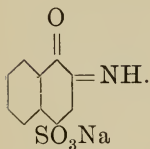
Dye-stuffs containing the OH groups in the ortho position with regard to the azo groups also exhibit the property of forming lakes with mordants.*

* E. Erdmann and O. Borgmann. Ger. Pat., 78,409; *Berl. Ber.*, Ref., 1895, p. 206.

Of the naphthalene series, the following are mordant

dye-stuffs : dioxynaphthoquinone, $\text{C}_{10}\text{H}_4 \begin{array}{c} (\text{OH})_2 \\ -\text{O} \\ | \\ -\text{O} \end{array}$, or

$\text{C}_{10}\text{H}_4 \begin{array}{c} \text{=O} \\ \text{=O} \end{array} \begin{array}{c} (\text{OH})_2 \\ \text{=O} \end{array}$, and derivatives of o. naphthoquinonimide, *e.g.*,



It is therefore evident that, as in the case of the origin of coloration already discussed, the property of dye-stuffs for forming lakes with mordants rests upon causes which we are not yet able to clearly define. The property in question is not merely due to the hydroxyl groups alone, since these can only give effect to their power in this respect when arranged in a certain way in the molecule, for which reason there are numerous dye-stuffs that contain hydroxyl groups without, however, being mordant dye-stuffs.

Dye-stuffs that contain neither hydroxyl nor carboxyl groups do not form lakes with mordants.

Finally, it may be remarked that dyeings produced by the use of mordant dye-stuffs are generally faster than those obtained from dyes alone.

FLUORESCENCE IN DYE-STUFFS.

Some dye-stuffs exhibit strong fluorescence when dissolved in different solvents. An attempt has recently been made by Richard Meyer to trace the connection between this property and the constitution of the dye-stuffs by which it is exhibited; and according to him the phenomenon is

attributable to the presence of certain groups which he calls "fluorophorous" groups. These comprise the pyrone ring, azine ring, the ring contained in anthracene and acridine, etc. Considerable influence, however, is also exerted by the substituents entering into the molecule of the dye-stuff, their position therein being the principal factor.

An observation in respect of fluorescence has also been made by O. Fischer and Hepp in the case of fluoresceine anilide.

TOXIC PROPERTIES OF DYE-STUFFS.

Among the laity it is a generally accepted opinion that all artificial dyes are poisonous. This prejudice has come down from the early period of aniline dye manufacture, at which time commercial fuchsine and all the colours derived therefrom were strongly contaminated with arsenic. At present, however, they are prepared in a condition perfectly free from arsenic, and for the most part are in themselves non-poisonous. Up till quite recently it had only been demonstrated that seven dye-stuffs (picric acid, Victoria Orange—saffron substitute—Aurantia, Coralline, Metaniline Yellow, Orange II. and Safranine) are capable of exerting toxic action when taken internally, Victoria Orange in particular being a very strong poison. Latterly, however, it has been found that a number of other dyes (Martius Yellow, Fast Yellow, Methyl Orange, Fuchsine and Acridine Red) induce serious disturbance of digestion, even in comparatively small quantities. Hence the use of coal-tar dyes for colouring food stuffs and delicacies is apparently not free from objection. In this connection unconditional prohibition should be laid on the employment of dyes such as Methylene Blue and Malachite Green, which, being double salts of zinc chloride, are capable of exerting a poisonous action in consequence of their zinc content.

A number of metallic pigments, such as vermilion, and the lead, copper, zinc and barium dyes, are well-known poisons; but these come under consideration in only a subordinate degree for the purposes in question.

USES OF DYE-STUFFS.

Apart from their principal application to the dyeing and printing of textiles, dye-stuffs find extensive and varied employment in the colouring of paper, straw, wood, grasses, flowers, leather, feathers, hair, fats, wax, soap, ink, fruit juices, liqueurs, delicacies (sweets, maccaroni, etc.) and varnishes. They are also used in the production of varnishes for coloured paper, carpet printing, lithographic printing and decorative painting.

Some of them are employed in *analytical chemistry* as indicators: Methyl Orange, Congo Red, Litmus, etc.

A number of nitro dye-stuffs, *e.g.*, picric acid (and picrates), dinitrocresol, dinitronaphthol, etc., are used as *explosives* and in the preparation of *smokeless powder*.

In consequence of their physiological action many dye-stuffs are employed as *curative agents*, chief among them being Methyl Violet, Auramine and Methylene Blue. Thanks to their powerful antiseptic properties and diffusibility, the two first-named—known as blue and yellow pyoctanine (pus destroyer)—are valuable medicaments, their application being, however, restricted on account of their disagreeable subsidiary staining action. Methyl Violet was first employed by Stilling as a bactericide in optical medicine, and afterwards in other special cases, its chief importance in surgery, however, being as a preventive of malignant new growths. The employment of auramine is of a very similar character.

Methylene Blue (as a free base) is principally used as an analgetic (anodyne) for internal application; but, in conse-

quence of its property of rapid diffusion through nervous tissue, it is also applied as an injection. It is used in cases of malaria, cancer, Bright's disease, etc.

Safranine, Lydine (Mauveine), Vesuvine, Aniline Blue, Carbofuchsine, Alizarine Yellow C (gallacetophenone), etc., have also been essayed as medicaments or antiseptics. The potassium salt of dinitro-orthocresol is put on the market by the Farbenfabriken vorm. Friedr. Bayer & Co., under the name of antinnonin, and has been found to act energetically on fungoid growths in cellars and as a remedy for dry rot.

Dye-stuffs are used in histology and bacteriology for *staining microscopical preparations*—especially Methylene Blue.

Some dyes are employed in *photography* to render the plates sensitive to the light they absorb—orthochromatic. Chief among these are: Cyanine, Quinoline Red, Eosine, Magdala Red, Coralline, Aldehyde Green, etc.

Finally, thanks to their high tinctorial powers, certain dye-stuffs have been applied to the purposes of *geographical research*. Thus, for instance, Fluoresceine, in the form of its fluorescent alkaline solution, was employed by A. Kop, of Basle, to investigate the existence of a connection between the Rhine (Lake Bodensee) and the Danube. In this experiment an alkaline solution of ten kilos. of Fluoresceine was poured into the Danube between Möhringen and Immendingen; at the end of sixty hours a decided fluorescence, which persisted for about thirty-six hours, was observed in the waters of the Ach, a small brook flowing into Lake Bodensee.

COAL TAR.

The dry distillation of wood, peat, lignite, coal, etc., furnishes, in addition to gas, an oily distillate darkened by

the presence of carbon, and well known by the name of *coal tar*. This is a product of extremely complex composition, the constituents being in part present in the raw material, and partly formed during distillation. It is a well-known fact that some organic bodies of simple composition are condensed to more complex forms at high temperatures, and that others of complex constitution are split up, under the same conditions, into more elementary forms.

In this manner aromatic compounds can be formed from bodies of the fatty series and *vice versâ*, the course of such pyrogenic reactions depending on the temperature, pressure, duration of heating and, above all, the nature of the substances employed. Consequently the body known as tar is of very variable composition, and substances rich in hydrogen and oxygen, like wood, peat and lignite, will furnish tar very different in composition to that yielded by coal, which is rich in carbon and poor in hydrogen; in the former case members of the fatty series will predominate, whilst in the latter more aromatic compounds are formed on distillation. As the aromatic bodies alone can be utilised in the manufacture of dye-stuffs, it follows that coal tar is the most suitable material for that purpose, and therefore will be the only class of tar considered here.

As far back as the seventeenth century the fact that coal furnishes tar on distillation was observed by Joachim Becher; and the presence of combustible gases was afterwards detected. This discovery remained unnoticed for a long time, and it was only at the end of the eighteenth century that attempts were made to produce *illuminating gas* by distilling coal. This gave rise to the gas industry, the foundation of which is generally attributed to William Murdoch; but the actual application of gas to lighting purposes was first carried out later by Winzler, after overcoming numerous obstacles.

After a portion of London had been lighted with gas in

1814, the manufacture of illuminating gas quickly spread on the Continent, the bye-product—tar—being however neglected; in fact it was regarded as an encumbrance, and was only used for subsidiary purposes, as fuel, paint, etc.; and only towards the middle of the nineteenth century did it begin to receive a larger share of attention. The first impulse in this direction was given by A. W. Hofmann, who, in 1845, detected the presence of benzol in coal tar; and soon afterwards his pupil, Mansfield, elaborated a process for the recovery of the benzol on a manufacturing scale. The process, however, did not attain any great importance until the discovery of the first artificial dyes, mauveine (1856) and fuchsine (1859), both of which were prepared from benzol. A commencement was now made at the fractional distillation of the tar, and a number of substances were isolated therefrom: benzol homologues, phenols, naphthalene and anthracene, which were soon utilised as the raw material for the production of a series of valuable dye-stuffs.

Notwithstanding the present great expansion of the dye-stuff industry, the production of tar is never attempted as a special branch of manufacture, sufficient being obtained as a bye-product in gas works. The yield varies from 3·5 to 6 per cent. of the weight of coal distilled.

Formerly the bulk of the coal tar used in Germany for the production of dye-stuffs was obtained from England, but the importation has now ceased. On the other hand England still supplies benzol, a large amount of naphthalene, the bulk of the anthracene, and almost all the carbolic acid used in Germany.

Of late the practice has arisen of superseding the old open coke ovens in ironworks, wherein the distillates were simply burned away, by enclosed stills which enable the coal tar to be recovered. The composition of coke tar is extremely variable, and chiefly depends on the kind of oven employed;

it is only of value for dye manufacture when formed at a high temperature, since that produced at low temperatures yields merely paraffin, etc. In contrast to gas tar, the tar from coke ovens contains, along with small quantities of naphthalene and carbolic acid, a relatively large proportion of anthracene.

According to S. Krämer,* the German coke factories produced, in 1896, about 5,000 tons of benzol, an amount that is certainly exceeded at the present day, the recovery of benzol and toluol from coke gases, by absorption in heavy oils, being a continually increasing practice. According to Brunck,† the total output of benzol and toluol in 1900 amounted to 25,000 to 30,000 tons, of which about four-fifths must be taken as representing benzol.

Of the total output of tar products (dye-stuffs, medicaments, etc.), about two-thirds are made in Germany, the remainder being produced in England, Switzerland, and France. In a private communication received from C. Duisberg, the value of these manufactures in Germany is fixed at the sum of 150 million marks (shillings) for the year 1900.

The undistilled tar is used as fuel, for gas-making, lamp-black manufacture, or as a paint for wood, masonry, roofing felt, metals, etc.; also for disinfection and a remedy against vermin (in agricultural districts), etc.

Another source, more particularly for benzol, is in the purification of lighting gas, from which the benzol can be recovered by washing with heavy oils.

Tar is also obtained by the distillation of lignite (brown coal), but the product differs from coal tar in containing no benzol or its homologues, the higher percentage of hydrogen and oxygen in the lignite causing the tar to contain a pre-

* *Chem. Zeit. Rep.*, **21**, p. 136.

† *Berl. Ber.*, 1900, No. 78.

dominating proportion of members of the fatty series. This, however, is not invariably the case, Heusler having detected the presence of considerable quantities of aromatic hydrocarbons in the tar from highly bituminous lignite from Saxony. These products can also be obtained from ordinary lignite tar by passing the vapours through red-hot pipes; and in a similar manner petroleum residues can also be utilised for the production of benzol.

COMPOSITION OF COAL TAR.

As already stated, coal tar is of variable and highly complex constitution. It contains water, hydrogen, nitrogen, cyanogen, carbon monoxide, carbon dioxide, hydrocyanic acid, sulphuretted hydrogen, ammonia; hydrocarbons of the fatty series, such as methane, ethane, acetylene, etc.; aromatic compounds like benzol and its homologues, naphthalene, anthracene, phenanthrene, fluorene, pyrene, chrysene, etc.; phenols, aromatic bases, such as pyridine, quinoline, quinaldine, aniline, picoline, lutidine, acridine, carbazol, etc., etc.

Altogether more than 100 substances have been found, with more or less certainty, in coal tar. The products of distillation include a gaseous, an aqueous, and an oily distillate, the latter alone—forming about 42 per cent. of the whole—containing the substances capable of utilisation in the production of dye-stuffs. These are:—

	Average yield per cent. of the weight of the tar.
Benzol	0·6-0·8
Toluol	0·2-0·4
Xylol	0·2-0·2
Crystallisable phenols	0·2-0·3
Cresols	0·5-0·8
Naphthalene	2-10
Anthracene	0·2-0·4

The chief use of the pyridine (0·02-0·04 per cent.) or the pyridine bases, boiling between 100 and 145° C., is for denaturing alcohol and for purifying anthracene. The quino-line (0·01 per cent.?) is only exceptionally recovered, and the comparatively large proportions of phenanthrene in the tar are rarely isolated. Aniline occurs merely as traces in coal tar.

THE FORMATION OF COAL TAR.

As already mentioned in the Introduction, the effect of high temperatures on organic substances is to convert some simpler compounds into more complex forms, and to change other complex bodies into simpler ones. Finally, given a sufficiently high temperature, there must be left behind such compounds as present the greatest amount of resistance to heat, *e.g.*, methane, ethylene, acetylene, benzol and its homologues, naphthalene, anthracene, phenanthrene, chrysene, carbazol, etc. Hence these compounds are everywhere met with when organic substances have been exposed to a very high temperature, and must, therefore, be contained in all gases and tars produced by dry distillation.

Of special importance to the theory of the formation of coal tar, or the substances therein contained, are the researches on hydrocarbons performed by Berthelot and others. In these experiments, the hydrocarbon vapours were passed through red-hot pipes, whereupon it appeared that aromatic compounds are produced from simple hydrocarbons of the fatty series by the elimination of hydrogen and by polymerisation; and that conversely the aromatic hydrocarbons can be converted into simpler hydrocarbons by the same means. Thus:—

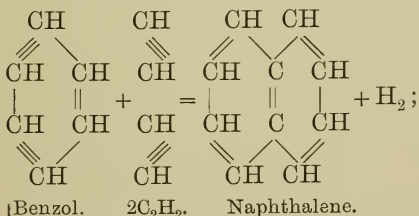
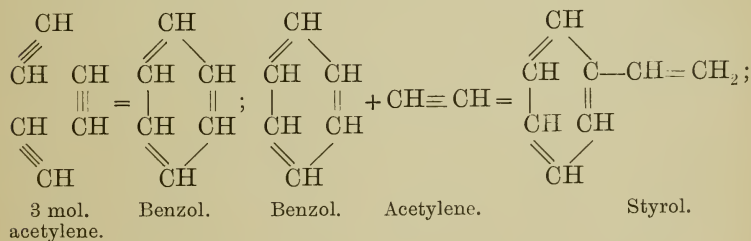
Methane can be converted into propylene, benzol and naphthalene.

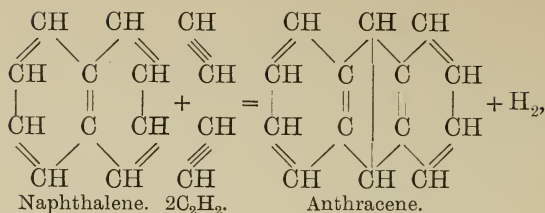
Acetylene can be converted into hydrogen, ethane, ethylene, benzol, styrol and naphthalene.

Benzol+ethylene can be converted into styrol, naphthalene, anthracene, etc.

From these experimental facts one may easily picture the manner in which the aromatic compounds in tar may have been formed. It must, however, be remarked that the Berthelot explanation—which has been further developed by R. Anschütz and others—is in any event too one-sided, other and more complex processes probably coming into play. Moreover, according to Heusler, aromatic hydrocarbons must be regarded—in part at least—as primary distillation products of the aromatic substances present in the coal.

In the formation of aromatic hydrocarbons, Berthelot ascribes a principal rôle to acetylene; benzol being formed by the condensation of three molecules of acetylene, whilst further condensation gives styrol, naphthalene, anthracene, etc., somewhat after the manner represented by the following formulæ:—



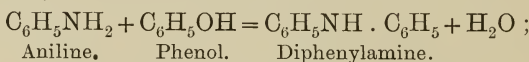


and so on.

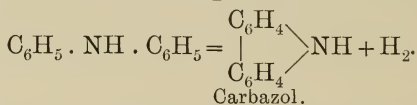
The *phenols* are probably formed direct from the raw materials, whilst the *primary* bases are elaborated from hydrocarbons or phenols and ammonia :—



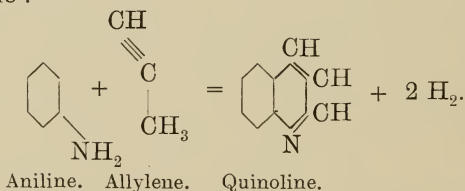
Secondary bases are probably formed from primary bases and phenols, or from the former alone :—



Further condensation may produce the stable *carbazols* :—



Quinoline may be pictured as being formed from aniline and allylene :—



Aldehydes also probably play some part in these pyrogenic reactions.

Finally, mention may be made of the circumstance that the detection of ethylbenzol in technical xylol by Noelting and Palmer has disproved the previously existing hypothesis that benzol derivatives with long lateral chains could not be produced in the tar-forming process.

THE DISTILLATION OF COAL TAR.

Before proceeding to dissociate coal tar into its constituents by distillation, the raw material must be freed from ammonia water as completely as possible, since the presence of this latter substance would have a highly injurious effect on the progress of distillation (causing frothing over). This separation is effected by gravitation in the tar cisterns, and when terminated the tar is transferred into the stills—upright retorts made of boiler plate and set in masonry. The tar is kept in motion in the stills by means of a stirring apparatus or by blowing in superheated steam, and direct fire heat is used. The escaping vapours, which at first consist of coal gas, ammonium carbonate, etc., are cooled by passing them through a coiled pipe immersed in a tank of water.

This first distillation effects merely a coarse separation into four fractions according to density. The first fraction, the so-called light oil, consists of the distillates passing over up to about 150°C . It has a lower density than water, and therefore floats on the surface of the latter, and it also contains benzol and its homologues, in addition to ammonia water and hydrocarbons of the fatty series.

The second distillate, which will not float on water but has almost the same density as that liquid, is collected separately as intermediate oil, and chiefly consists of carbolic acid and naphthalene. When the latter commences to pass over, the cooling water surrounding the coil must be warmed to prevent obstruction resulting from the crystallisation of the naphthalene. This fraction boils somewhere between 150 and 200°C .

After the intermediate oil comes the heavy oil, *i.e.*, the distillate of higher density than water, and therefore sinking therein. Here are contained naphthalene, higher boiling

phenols, quinoline bases, etc. The fraction is collected up to about 300° C.

The next succeeding distillate is anthracene oil, or, as it is generally termed from its colour, green oil. This contains the anthracene. Distillation is not pushed beyond about 400° C., the subsequent fractions containing merely inutilisable substances, such as chrysene, pyrene, etc., and a small proportion of anthracene.

Of late anthracene has become so cheap (about 2d. per lb.) that many distillers have ceased to recover it.

Towards the end the distillation is effected with steam, the result of which is to hasten distillation and thus shorten the period of exposure of the hydrocarbons to the high temperature, also to protect the bottom of the still from caking.

The residue from the distillation is pitch, which is utilised in the preparation of briquettes, asphalt paving, roofing felt, varnishes, iron paint, etc.

PURIFYING THE DISTILLATES.

After the preliminary separation of the tar into four fractions has been accomplished, these latter are purified by repeated fractional distillations, washing with acids and alkalis, crystallisation, and also by cold and warm pressing.

The fractional distillation is effected in the Savalle* columnar still, which resembles the apparatus used in the manufacture of spirit.

The object of the (sulphuric) acid treatment and alkali (caustic soda) treatment is to separate the hydrocarbons insoluble in these solvents from the admixed pyridine and quinoline bases (and other basic substances) as well as

* Dingler, *Polyt. Journ.*, 1877, **223**, p. 615.

phenols. This is accomplished in upright lead-lined iron cylinders.

Pressing is a very suitable means for separating the naphthalene and anthracene—which crystallises out on cooling the corresponding fractions—from adherent particles of oil. The operation is performed in filter presses, and also with the aid of hydraulic pressure assisted by warmth.

The light oils are treated for the recovery and purification of benzol, toluol and xylol by fractional distillation, followed by washing with acid and alkali, then very carefully fractionated a second time, so that finally the benzol and toluol at least are obtained perfectly pure. On the other hand, the three xylols are not separated. In some establishments the three xylols are not isolated at all, but are mixed with other constituents boiling between 100 and 200° C. and sold as solvent naphtha. Of this substance two kinds are known in commerce, the one distilling below 160° C., the other between 160 and 190° C. Sometimes also it is unnecessary to completely separate the benzol and toluol (see Intermediate Products).

The naphthalene deposited from the oils passing over between 180 and 250° C. is first pressed, then washed, distilled, pressed again (warm), and finally re-distilled or sublimed.

The anthracene, which is deposited as a green fatty mass from the anthracene oils, is first freed from the bulk of the mother liquor by pressing. This gives a 12 to 15 per cent. product, which is increased to 30 per cent. strength by a second hot pressing.

This is ground and extracted with solvent naphtha, which operation dissolves out nearly the whole of the impurities and but a small portion of the anthracene itself, and even this is deposited almost completely on cooling the solution. The (now 40 per cent.) anthracene is not purified any

further, but is sold to the dye manufacturers, who work it up into anthraquinone (see Alizarine). According to recent patents the employment of liquid sulphurous acid or acetone oils for extracting 30 to 40 per cent. anthracene furnishes an 85 to 90 per cent. product, nearly the whole of the anthracene remaining undissolved. A still better but more expensive purifying agent is pyridine, which, after the second treatment, gives a 95 to 98 per cent. product. In order to render anthracene fit for working up into anthraquinone it must be reduced to a very fine state of division, an object accomplished by sublimation with steam.

Finally, the phenols also are isolated from the tar distillates. Of these substances carbolic acid is the most important, and this is recovered by extraction with caustic soda from the so-called creosote oils forming the intermediate runnings between the light and intermediate oils. The solution is first freed from hydrocarbons by the aid of heat, then treated with hydrochloric acid, which throws down the crude carbolic acid as an oil. This is then fractionated, and afterwards crystallised by cooling. The crystals are centrifugalised and again fractionated.

In consequence of the present high price of carbolic acid, and the low rates prevailing for benzol, some works have commenced to prepare the former by synthetic means.

Phenols, cresols, etc., of high boiling point have long been used, in a very impure state, for impregnating wood, and as disinfectants. More recently, the coal-tar fractions boiling at about 200° C., and chiefly containing cresols, have been put on the market in the form of solutions in resin or fatty soaps, under various names, such as: Sapocarbol (Schenkel, 1884), Creolin (Pearson, 1887), Lysol (Damman, 1890), Solveol and Solutol (Heyden), etc., for use as disinfectants, for which purpose their solubility or capacity for forming emulsions renders them suitable.

BIBLIOGRAPHY.

For a more exhaustive account of the subject dealt with in the present chapter, see :—

G. Lunge, *Die Industrie des Steinkohlentheers und Ammonia* (Coal Tar and Ammonia Industry).

G. Schultz, *Die Chemie des Steinkohlentheers* (The Chemistry of Coal Tar), 2nd ed., vol. i.

INTERMEDIATE PRODUCTS IN THE
MANUFACTURE OF DYE-STUFFS.

Dye-stuffs cannot be manufactured direct from the hydrocarbons obtained from the distillation of coal tar, a previous conversion into other so-called “intermediate” products being necessary, *viz.*: amido bodies, phenols, sulpho acids, etc. Of these there is a large number, notwithstanding the limitation imposed by the low selling price.

In the early days of the coal-tar dye industry, the separation of the benzol and its homologues was only partially effected, and little importance was attached to the purification of the other distillation products. It was soon, however, discerned that impurity in the raw materials had an unfavourable influence on the results of the processes of manufacture, both as regards quality and quantity, and hence nowadays the raw materials are prepared in as pure a state as possible. This is an easy matter in the case of benzol and toluol; but in the higher homologues the difficulties have not yet been overcome. Still more difficult is the preparation of the nitro and amido compounds of these hydrocarbons, owing to the circumstance that, in the production of these derivatives, a number of isomers are always formed from each hydrocarbon.

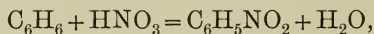
The two chief operations in the production of substitution products of the hydrocarbons are: (1) Nitration; (2) Sulphonation.

Nitration generally consists in a treatment with a mixture of concentrated nitric acid and sulphuric acid; sulphonation is effected with concentrated sulphuric acid, with or without anhydride, at different temperatures. Occasionally, for the introduction of several nitro groups, it is advisable to treat with sulphuric acid first, and then enter the resulting sulpho acids in concentrated nitric acid, whereby the SO_3H groups are entirely or partly replaced by NO_2 groups (see Nitro Dye-stuffs).

Pictet's observation that the progress of nitration is occasionally modified to a considerable extent by very low temperatures has not yet been put to any practical use.

The operations in question are conducted in cast-iron vessels, fitted with stirrers.

The nitration of benzol furnishes nitrobenzol,



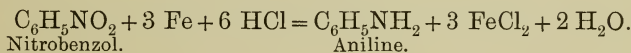
which is utilised partly as such (*e.g.*, in the preparation of fuchsine; as oil of mirbane in perfumery, etc.), but chiefly in the production of aniline. The nitration of toluol furnishes all three theoretically possible nitrotoluols, chiefly the ortho and para products, the meta derivative being formed in only small amount. These are then generally separated, mainly for the purpose of utilising the orthonitrotoluol for the production of the valuable o. toluidine or o. nitrobenzaldehyde by distillation *in vacuo* and congealing the solid p. nitrotoluol. According to a report by the Clayton Aniline Co., the separation can also be effected by treatment with alkaline sulphides, whereby the p. nitrotoluol is more readily reduced to the corresponding amido compound than is the case with the ortho derivative. This method, however, is not pursued on a large scale.

Nitration is a more complex operation in the case of xylol, on account of the larger number of isomeric nitro products then formed. All the three theoretically possible xylols, $C_6H_4(CH_3)_2$, occur in coal tar; but as the nearness of their boiling points precludes their separation they have therefore to be nitrated together.

The employment of all these substances as such in the manufacture of dye-stuffs is very restricted; they are in reality only the means for arriving at the corresponding valuable amido derivatives, aniline, o. and p. toluidine and the xylidines, which are the most valuable of all the intermediate products.

The conversion of the nitro bodies into the corresponding amido compounds is effected by reduction, with the assistance of ground cast-iron filings and hydrochloric acid. This is the modification, for manufacturing on the large scale, of the Béchamp method of amidising with iron filings and acetic acid. In this manner nitrobenzol is converted into aniline, the most valuable of all the intermediate products, and from which the artificial dye-stuffs derive their name of "aniline dyes," though this designation is not altogether appropriate, seeing that a not inconsiderable number are prepared without aniline.

This reduction process may be expressed by the following equation :—

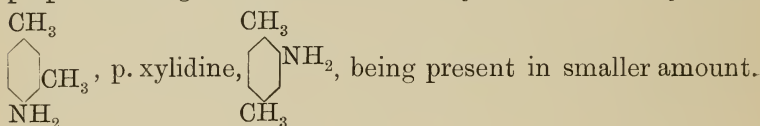


In practice, however, a smaller proportion of HCl is sufficient. According to A. Wohl the progress of the reaction is as follows: The reduction is mainly effected by the finely divided moist iron, which is converted direct into ferric hydroxide. This unites with the resulting ferrous chloride to form a basic salt, which in turn is converted by the metallic iron (in presence of ferrous chloride) into ferro-ferric oxide.

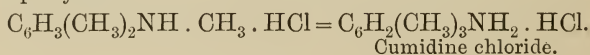
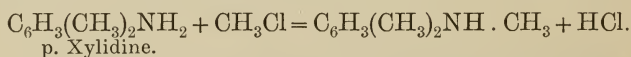
On subjecting to the same treatment the technical nitro-

toluol, which contains 70 per cent. of the ortho and 30 per cent. of the para derivative, a mixture of ortho- and paratoluidine is obtained. The former is an almost colourless, highly refractive liquid, whilst the latter forms crystals melting at 45° C. The substance now put on the market as "aniline oil," or "blue oil," is pure aniline; the "aniline for red" is a mixture in almost molecular proportions of aniline, o. toluidine, p. toluidine (slightly less) and a little xylidine. At the present time it has nearly gone out of use, consumers preferring to buy the pure aniline oil (blue oil) and toluidine separately. "Aniline for safranine" is a mixture of aniline and o. toluidine recovered—under the name of *échappés*—as a distillate on fusing fuchsine.

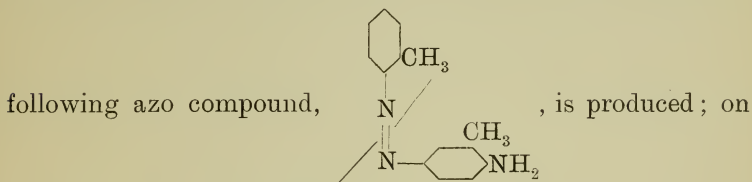
The chief constituent of "technical xylol" is the meta derivative, p. xylol being present in smaller amount, and o. xylol only in minute proportion. This mixture on nitration and reduction furnishes "technical xylidine," which consists of five isomeric amido compounds. The preponderating member is the asymmetric m. xylidine,



These are principally used for the production of scarlet azo dye-stuffs, for which purpose the asymmetric m. xylidine is best adapted. It is obtained by crystallising the acetic acid salt. Still more vivid dyes are obtained from ψ cumidine, which in turn is best prepared from p. xylidine. For this purpose the general method of Hofmann and Martius is employed, wherein the methyl first introduced into the amido group enters into the nucleus by a process of atomic migration in the molecule:—



Another method of producing amines consists in the dissociation of azo compounds by the aid of zinc dust. *Example*: By the action of nitrous acid on o. toluidine the



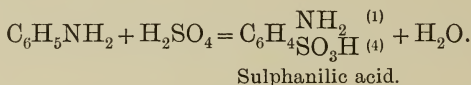
treating this with zinc dust it is split up in the direction of the sloping line, and furnishes a mixture of o. toluidine and p. toluenylenediamine. These basic mixtures are employed in the manufacture of safranines.

All the various above-mentioned amines are principally employed as such in the manufacture of dye-stuffs. Some of them, however, are nitrated, sulphonated, alkylated, etc. Two methods of nitration are practised. The older process consists in the indirect introduction of the NO_2 group; aniline, for example, being nitrated as acetanilide, whereby ortho- and para-nitracetanilide are produced, the nitrated amine being then recovered by eliminating the acetyl group. The nitration of benzylidenaniline ($\text{C}_6\text{H}_5\text{N}=\text{CH}.\text{C}_6\text{H}_5$) furnishes the para derivative almost exclusively. The meta-nitraniline unobtained by this method can be prepared by the partial reduction of m. dinitrobenzol, though a better way is by the new method of Hübner and Frerichs—dissolving the amine in concentrated sulphuric acid and then treating with fuming nitric acid in a refrigerating mixture. The product chiefly consists of meta derivatives.

p. Nitramines are particularly valuable on account of the good properties of the azo dye-stuffs produced with their assistance. The most important is p. nitraniline (see Nitraniline Red).

The treatment of amines with concentrated sulphuric

acid furnishes various sulpho acids, according to the concentration of the acid and the degree of temperature employed. Of the three theoretically possible sulpho acids of aniline the para compound, the so-called sulphanilic acid, is the most important. This is formed when aniline is heated with sulphuric acid, or better still on heating acid aniline sulphate alone :—

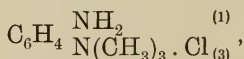


Similar behaviour is exhibited by the toluidines and xylidines, the sulpho acids of which, however, have only been partly investigated.

On heating aniline with methyl alcohol and hydrochloric acid or sulphuric acid the two hydrogen atoms of the amido group are displaced by methyl, and the important dimethylaniline, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, is obtained. Diethylaniline is prepared in the same manner. The action of nitrous acid on dimethylaniline in presence of a cooling mixture furnishes nitrosodimethylaniline, $\text{C}_6\text{H}_4 \overset{\text{N}(\text{CH}_3)_2^{(1)}}{\underset{\text{NO}^{(4)}}{\text{N}}}$, so largely used in the manufacture of dye-stuffs.

Latterly, *inter alia*, secondary derivatives of o. toluidine are also produced, *e.g.*, $\text{C}_6\text{H}_4 \overset{\text{CH}_3}{\underset{\text{NH}}{\text{N}}} \cdot \text{C}_2\text{H}_5^{(1)}$, which exhibit the interesting property of behaving in many respects like tertiary amines.

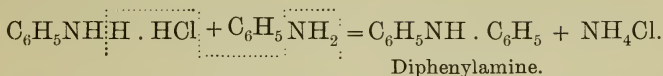
The methylation and subsequent reduction of the nitramines furnishes amidoammonium bases, *e.g.*,



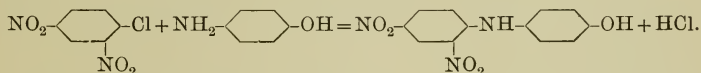
which serve in the preparation of the so-called Janus dyes (*q.v.*).

When aniline is heated with aniline chloride under pressure, one atom of hydrogen in the amido group is

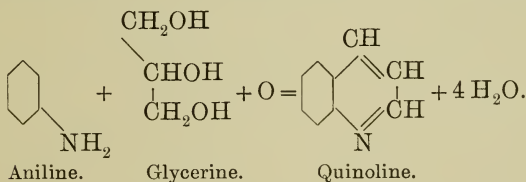
displaced by phenyl, the result being the formation of diphenylamine :



Quite recently a considerable degree of importance has been attained by a series of diphenylamine derivatives in connection with the manufacture of the so-called "sulphur dyes" (*q.v.*). These are generally produced by heating an aqueous or alcoholic solution of an amine with a chlorine derivative, in presence of a neutralising agent like sodium acetate, for combining with the liberated hydrochloric acid, *e.g.* :—



When aniline is heated with glycerine and sulphuric acid in presence of nitrobenzol, quinoline is formed :—*

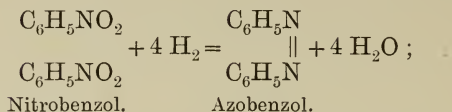


The value of this "Skraup's" synthesis resides in the circumstance that it is capable of general application (see Alizarine Blue). Up to the present, quinoline is not used in the manufacture of dye-stuffs (see Quinoline Dyes).

Whereas, as we have seen, the reduction of nitrobenzol in an *acid* solution furnishes aniline, the progress of the reaction is quite different in the case of an alkaline solution.

* It is assumed that this reaction first produces acrolein from the glycerine, and that this condenses with the aniline to form acroleinaniline, $\text{C}_6\text{H}_5\text{N}=\text{CH}-\text{CH}=\text{CH}_2$. The nitrobenzol acts merely as an oxidising agent.

On treating nitrobenzol with zinc dust and caustic soda, at boiling heat, the product first formed is azobenzol :

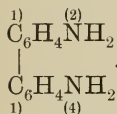


the further action of hydrogen converts the latter into hydrazo-

benzol : $\begin{array}{c} \text{C}_6\text{H}_5\text{NH} \\ | \\ \text{C}_6\text{H}_5\text{NH} \end{array}$; and when this is treated with acids, there

results, in consequence of molecular rearrangement, benzi-

dine, * $\begin{array}{c} \text{(1)} \quad \text{(4)} \\ \text{C}_6\text{H}_4\text{NH}_2 \\ | \\ \text{C}_6\text{H}_4\text{NH}_2 \\ \text{(1)} \quad \text{(4)} \end{array}$, together with the isomeric diphenylene,



The first plays an important part in the manufacture of the benzdine dyes.

In a similar manner the also very important o. toluidine,

$\begin{array}{c} \text{(3)} \\ \text{CH}_3 \\ / \\ \text{(1)} \text{C}_6\text{H}_3 - \text{NH}_2 \text{(4)} \\ | \\ \text{(1)} \text{C}_6\text{H}_3 - \text{NH}_2 \text{(4)} \\ \backslash \\ \text{CH}_3 \text{(3)} \end{array}$, is formed from o. nitrotoluol ; and dianisidine,

$\begin{array}{c} \text{(3)} \\ \text{OCH}_3 \\ / \\ \text{(1)} \text{C}_6\text{H}_3 - \text{NH}_2 \text{(4)} \\ | \\ \text{(1)} \text{C}_6\text{H}_3 - \text{NH}_2 \text{(4)} \\ \backslash \\ \text{OCH}_3 \text{(3)} \end{array}$, from o. nitranisol.

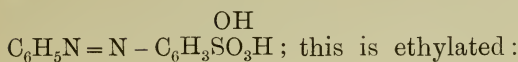
Of a far more complex character is the production of asymmetric benzdine bases, as an example of which the preparation of Weinberg's † ethoxybenzdine may be cited.

In this method phenol is sulphonated : $\text{C}_6\text{H}_4\text{SO}_3\text{H}$; the

* "Electrolytic Process," *Berl. Ber.*, 1900, p. 2329.

† Ger. Pat., No. 44,209 (A. Weinberg), *Berl. Ber.*, xx., p. 3171.

action of diazobenzol then forms therefrom the azo dye :



and is reduced, analogous to the formation of benzidine (see above), transposed, and finally the sulpho group is eliminated.

Heating benzidine with fuming sulphuric acid furnishes benzidine sulphone,* $\text{SO}_2 \begin{array}{c} \diagup \text{C}_6\text{H}_3-\text{NH}_2 \\ | \\ \diagdown \text{C}_6\text{H}_3-\text{NH}_2 \end{array}$, which on being heated

further is converted into a disulpho acid, $\text{SO}_2 \begin{array}{c} \diagup \text{C}_6\text{H}_2\text{NH}_2 \\ | \\ \diagdown \text{C}_6\text{H}_2\text{NH}_2 \\ \diagdown \text{SO}_3\text{H} \end{array}$.

These compounds, also, are used in the production of benzidine dye-stuffs (sulphonazurines).

OTHER REDUCTION PROCESSES.

The great dependence of the course of a reaction upon the prevailing conditions can be gathered in a very instructive manner from a series of methods that have latterly come into use for the reduction of nitro compounds.

E. Bamberger† and A. Wohl‡ simultaneously and independently arrived at the great discovery that the reduction of nitrobenzol with zinc dust in a neutral solution furnishes a hitherto unknown compound, phenyl-hydroxylamine, $\text{C}_6\text{H}_5\text{NHOH}$.

According to Kalle & Co., § a very good yield of this substance is obtained by allowing the reaction to proceed in the cold and in presence of an aqueous solution of an

* *Ber. d. d. Chem. Ges.*, xxii., p. 2459 (1889), P. Griess and C. Duisberg.

† *Berl. Ber.*, 27, pp. 1347 and 1548.

‡ *Ibid.*, 27, p. 1432.

§ Ger. Pat., No. 89,978.

ammonia salt. The high reactive power of phenylhydroxylamine, which is readily oxidised into nitroso derivatives, condensed with aldehydes, and transposed into p. amidophenols by acids, has not as yet, however, led to any technical application of this substance.

The reduction of nitro compounds in concentrated solution in sulphuric acid, by zinc, results in amidophenols.

The electrolytic process of reduction furnishes highly divergent products, according to the conditions under which the reaction is conducted. Thus, in the case of concentrated sulphuric solution, amidophenols* are formed, whilst under other conditions, azoxy, azo, hydrazo, and amido compounds are produced.

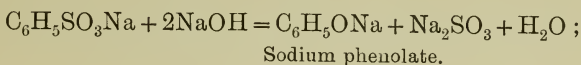
In many instances the use of bisulphite affords a suitable means for the conversion of nitro compounds into amido compounds, sulphonation, however, frequently occurring at the same time. Thus, for instance, nitrobenzoic acid furnishes amidosulphobenzoic acid (Ger. Pat., Application W., 14,921); α -nitronaphthalene gives, as chief product, 1. naphthylamine- 2. 4.-disulpho acids; dinitronaphthylenes yield naphthylenediamine sulpho acids, etc.

The second principal method for producing benzol derivatives, used in the dye-stuff industry, is that of sulphonation.† This is the usual way for the recovery of the hydroxyl derivatives; but the sulpho acids are also employed, as such, in the manufacture of dye-stuffs—that is to say, not those of the aromatic hydrocarbons, but those of the phenols, amines, etc. The sulphonation of benzol may be given as an example: When benzol is allowed to

* Fr. Bayer & Co., Ger. Pat., No. 75,260, *Berl. Ber.*, 1894, p. 821.

† Wendt found that infusorial earth and animal charcoal produce similar effects of condensation to that of platinum black on gases; so that in presence of these substances the action of cold concentrated sulphuric acid is often equal to that of hot or fuming sulphuric acid.

run into fuming sulphuric acid, benzolmonosulphonic acid— $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ —is the product first formed. On fusing this with caustic soda, we obtain the phenol:



the free phenol being then separated from the sodium compound by the action of an acid. True, the phenol is mainly recovered from coal tar, but owing to its present high price is also prepared from benzol by the method just described.

Further sulphonation converts the benzolmonosulphonic acid into the meta disulphonic acid, which, on fusion with caustic soda, furnishes resorcine, the most important of the three dioxybenzols.

Fusing with soda is consequently the means invariably employed for replacing the SO_3H group by the HO group in aromatic bodies.

In some instances the introduction of the sulpho group can be more advantageously effected with the aid of bisulphite; thus, for example, the sulpho acid of p. phenylenediamine is obtained by treating this amine with bisulphite (E. & H. Erdmann), that of dinitrobenzol by the action of sulphite on dinitrochlorobenzol.

An entirely original method of introducing hydroxyls has been recently discovered (Bohn, Schmidt)—namely, by treating with sulphuric acid very rich in anhydride.

Of other new methods for introducing OH groups, or for the production of phenols, mention may be made of the following, although they have not as yet attained any degree of technical importance.

Wiedel* found that phloroglucine can be obtained by the hydrolysis of symmetrical triamidobenzol (the method has been patented by L. Cassella).

* E. Flesch, *Monatssh. f. Chem.*, vol. xviii., p. 755.

On dissociating the 1. 3. naphthalene derivatives with alkalis at high temperatures, o. toluylic acid ($\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH}^{(1)} \\ \text{CH}_3^{(2)} \end{smallmatrix}$), or its derivatives, can be produced. This method, applied to 1. 3. 6. naphthalenetrisulphonic acid, furnishes m. cresol, which was hitherto difficult to prepare.

According to K. Elbs,* phenol is converted into hydroquinone by the action of persulphates on an alkaline solution in the cold; should the para position be occupied, pyrocatechin results.

According to a report by Thiele,† quinone is transformed into (acetylated) oxyhydroquinone by acetic anhydride.

The nitration of the phenols furnishes nitrophenols, which can be converted into amidophenols by reduction. Latterly, secondary and tertiary amidophenols—chiefly those belonging to the meta series, *e.g.*, $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \begin{smallmatrix} \text{OH}^{(1)} \\ (3) \end{smallmatrix}$ —have been produced, the latter finding employment in the manufacture of rhodamines.

On alkylation (with methyl chloride or salts of ethylsulphuric acid) the nitrophenols yield nitrophenol ethers, *e.g.*, nitranisol, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OCH}_3^1 \\ \text{NO}_2 \end{smallmatrix}$, and nitrophenetol, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{NO}_2 \end{smallmatrix}$. The same bodies are also obtained from the nitrochlorobenzols by boiling with potassium methyl- or ethyl-alcoholate.

The reduction products of the nitranisols and nitrophenetols, *viz.*, the anisidines and phenetidedines, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{Alkyl}^1 \\ \text{NH}_2 \end{smallmatrix}$, are employed in dye-stuff manufacture (azo dyes). Some of their derivatives are used in medicine, *e.g.*, phenacetine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{C}_2\text{H}_5^{(1)} \\ \text{NH} \cdot \text{C}_2\text{H}_3\text{O}^{(4)} \end{smallmatrix}$, and phenocoll, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{C}_2\text{H}_5 \\ \text{NH} \cdot \text{COCH}_2 \cdot \text{NH}_2 \end{smallmatrix}$.

The sulphonation of the phenols furnishes the phenolsul

* *Zeits. angew. Chem.*, 1897, p. 171.

† *Berl. Ber.*, 1898, p. 1247.

phonic acids; phenol itself yields ortho- and para-phenolsulphonic acid.

These find employment both in the manufacture of dye-stuffs and in medicine, o. phenolsulphonic acid being sold under the names sozolic acid and aseptol; whilst salts of di-iodoparaphenolsulphonic acid are put on the market by Trommsdorff as soziodols.

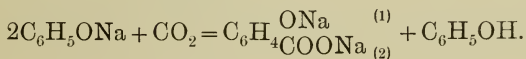
Nitrosophenols are used as dye-stuffs.

It frequently happens that dye-stuffs containing a phenol exhibit great susceptibility to the action of alkalis. In order to remove this defect, the hydroxyl group is alkylated, not in the phenol itself, but in the finished dye-stuff (see Chrysophenine).

The following carbo acids of benzol and its homologues are used in the manufacture of dye-stuffs: benzoic acid, salicylic acid, creosotic acid, gallic acid, phthalic acid, and tannic acid.

Benzoic acid is obtained either by heating benzol trichloride ($C_6H_5CCl_3$) with water, in presence of an iron compound, without pressure, or by the oxidation of toluol with manganese dioxide and sulphuric acid. Nitration chiefly furnishes meta-nitrobenzoic acid; whilst reduction gives the corresponding amidobenzoic acid, which is used as a constituent of dye-stuffs.

Salicylic acid, which is now largely used in medicine and as a component in the production of mordant azo dyes, is prepared by the Kolbe method: conducting heated carbon dioxide over sodium phenol:



In this reaction the first product is sodium salicylate, $C_6H_5O.COONa$.

Salicylic acid is largely used medicinally, chiefly in the form of the sodium salt, or as the acetyl compound sold as

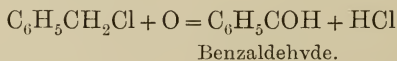
aspirine. By fusing salicylic acid with phenol and heating the mixture with phosphorus oxychloride, Nencki obtained the phenylate of salicylic acid, $\text{C}_6\text{H}_4\text{COO} \cdot \text{C}_6\text{H}_5$, which, under the name of salol, is also used in medicine.

Creosotic acids are prepared from cresoles in the same manner as salicylic acid from phenol.

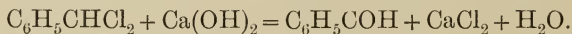
Gallic acid is recovered by boiling gallotannic acid with dilute sulphuric acid. This latter, also known as tannic acid, or tannin, is obtained from gall nuts by extracting the powdered nuts with ether and alcohol, and dissolving the tannic acid from the extract by shaking it up with water.

Finally, phthalic acid was formerly prepared by oxidising naphthalene or its derivatives with nitric acid or chromic acid. However, the attempt to render Heumann's indigo synthesis technically useful has led to a new and very cheap method of preparing phthalic acid, consisting in the application of heat (to about 300°C.) to naphthalene and sulphuric acid in presence of mercury or a mercury salt, whereupon phthalic acid, in the form of anhydride, passes over as a sublimate. The chief part of the sulphuric acid in this reaction is that of an oxidising agent (Ger. Pat., 91,202); it is reduced to sulphurous acid, which in turn is converted into sulphuric anhydride by the Winkler method: mixing with air and passing over platinised asbestos.

The only important member of the aromatic aldehydes is benzaldehyde (oil of bitter almonds). This is prepared by heating benzyl chloride ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$) with lead nitrate and water, or by heating benzal chloride ($\text{C}_6\text{H}_5\text{CHCl}_2$) with lime:—



Benzaldehyde.

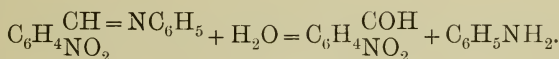


It is also formed, and that too in large quantities, on the

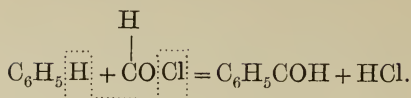
oxidation of toluol with manganese dioxide (Weldon sludge) and sulphuric acid.

Inter alia, benzaldehyde is used for the preparation of malachite green. Of its nitro compounds the only one that can be easily prepared by direct nitration is the meta derivative. This on reduction furnishes the amido compound; and on replacing the NH_2 group in this latter by OH (by diazotisation followed by boiling with water) we obtain the oxybenzaldehyde, so important for the preparation of dye-stuffs of the patent blue group.

Still more important is o. nitrobenzaldehyde, which is utilised in the production of indigo (M. L. Br.) and indigo salt (K.). According to Homolka it is prepared by condensing o. nitrobenzyl chloride $\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2\text{Cl}^{(1)} \\ \text{NO}_2^{(2)} \end{smallmatrix}\right)$ to the corresponding benzyl compound $\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_5 \\ \text{NO}_2 \end{smallmatrix}\right)$ with aniline, and then oxidising this product into o. nitrobenzylidene-aniline $\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}=\text{N} \cdot \text{C}_6\text{H}_5 \\ \text{NO}_2 \end{smallmatrix}\right)$. This latter on being treated with acids readily splits up into o. nitrobenzaldehyde and aniline:—



Of late a whole series of methods of preparing aldehydes have been made known, chief among them being the beautiful Gattermann processes. The first of these processes consists in passing dry carbon monoxide and hydrochloric acid gas (at 60 to 70° C.) through a mixture of cuprous chloride and aluminium chloride with the aromatic hydrocarbon into which it is desired to introduce the aldehyde group. Under these conditions (*i.e.*, in presence of cuprous chloride) the mixture of carbon monoxide and hydrochloric acid apparently behaves similarly to the non-existent formic chloride, and like other acid chlorides reacts on the hydrocarbon:—



In the second and for practical purposes more important method of Gattermann the phenols are treated with hydrocyanic acid and hydrochloric acid in presence of aluminium chloride. This produces at first aldimides (characterised by



the group $-\overset{\text{H}}{\underset{|}{\text{C}}}=\text{NH}$), which for the most part are dissociated into aldehyde and ammonia by the action of water. In some cases zinc chloride may be advantageously substituted for aluminium chloride, and oftentimes the reaction will proceed in the absence of any condensing reagent. This method furnishes still better results with the naphthalene series than with the benzol series, and has been employed by its inventor in a number of beautiful synthetic operations (daphnetine, aesculetine, asarone, etc.).

A second method of introducing the aldehyde group is based on the discovery by the Badische Anilin- und Soda-fabrik and by Gilliard, Monnet & Cartier that the CH_3 group in aromatic compounds can be easily oxidised to aldehydes by manganese dioxide and sulphuric acid. This method is employed in practice for the preparation of benzaldehyde from toluol, and of o. nitrobenzaldehyde from o. nitrotoluol. Finally, it has been found by the Geigy Co. that the old Reimer method—boiling with chloroform and alkali—for introducing the aldehyde group gives results of technical utility in the case of several naphtholsulphonic acids.

Mention may also be made of the following special methods :—

Kalle & Co. prepare from phenylhydroxylamine and formaldehyde an anhydro compound which furnishes p. amidobenzaldehyde on boiling with water. A similar method has also been patented by Geigy.

Para-amidobenzaldehyde can be prepared from both p. nitrobenzylaniline and p. nitrotoluol by fusion with sulphur and alkali sulphide. In the former case amidobenzyliden-aniline is first formed, which is then split up into aldehyde and aniline in the usual manner (see above). Similarly, o. amidobenzaldehyde can be produced from o. nitrobenzylaniline (M. L. Br.).

Finally, aldehydes can also be obtained by oxidising stilbene derivatives with potassium permanganate. Stilbene-sulphonic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{---CH=CH---} \\ \text{SO}_3\text{H} \end{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, furnishes o. sulphobenzaldehyde $\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COH}^{(1)} \\ \text{SO}_3\text{H}^{(2)} \end{smallmatrix} \right)$, which finds employment in the manufacture of dyes of the Patent Blue class.

Of the ketones, a considerable part is played by tetramethyldiamidobenzophenone, $\text{CO} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4\text{N}^{(1)}(\text{CH}_3)_2^{(4)} \\ \diagdown \text{C}_6\text{H}_4\text{N}^{(1)}(\text{CH}_3)_2^{(4)} \end{smallmatrix}$, a derivative

of benzophenone. This compound has the character of a base, and is produced when the chloride of dimethylamidobenzoic acid, resulting from the reaction of dimethylaniline and phosgene (COCl_2), is allowed to act on dimethylaniline. On reduction it furnishes the product tetramethyldiamido-

benzhydrol, $\text{CH} \cdot \text{OH} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4\text{N}^{(1)}(\text{CH}_3)_2^{(4)} \\ \diagdown \text{C}_6\text{H}_4\text{N}^{(1)}(\text{CH}_3)_2^{(4)} \end{smallmatrix}$, which is also used in the manu-

facture of dye-stuffs. This product may, however, be better prepared by oxidation, from the tetramethyldiamidodiphenyl-

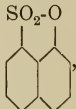
methane, $\text{CH}_2 \begin{smallmatrix} \diagup \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \\ \diagdown \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \end{smallmatrix}$, produced by the condensation of formaldehyde and dimethylaniline.

The operation of chlorination also plays a considerable part in the chemistry of colours. It is chiefly employed for the preparation of benzylchloride, benzalchloride, and benzotrichloride, from toluol, and for the production of the chlorobenzols, from which o. and p. chloronitrobenzol and dinitrochlorobenzol are obtained.

Almost as important to modern colour chemistry as the above-mentioned benzol derivatives are certain of the naphthalene derivatives, *viz.*: α - and β -naphthol, α - and β -naphthylamine, amidonaphthols, dioxynaphthalene, and a large number of the most divergent sulpho acids of these bodies. By far the greater number of these were sought for and discovered subsequent to the discovery of the benzidine dyes, and even now play their most important part in this group of dye-stuffs. In this connection particular interest attaches to the derivatives

in the 1. 8. or peri position $\left(\begin{array}{c} 8 \quad 1 \\ \text{ } \end{array} \right)$. They exhibit in a

high degree the properties of several of the ortho derivatives of the benzol series, *e.g.*, the tendency to the formation of

internal anhydrides. Thus, a naphthosulphone, , has

been prepared from 1. 8. naphtholsulphonic acid. Several of the sulpho acids of 1. 8. dioxynaphthalene can be employed for the direct dyeing of sheep's wool by being converted into dye-stuffs on the fibre, under the oxidising influence of chromates. For example, 1. 8. dioxynaphthalene 3. 6.-disulphonic acid, sold under the name Chromogene I. (M. L. Br.), dyes wool brown, and 1. 8. dioxynaphthalene-2. 4.-disulphonic acid acts as a black dye.

The raw material for all these bodies is formed by coal-tar naphthalene. As in the case of benzol, here also

nitration and sulphonation are the chief operations for producing the valuable naphthols, naphthylamines, and their sulpho acids. The dye-stuff components of the naphthalene series contain OH, NH_2 , SO_3H groups and chlorine as substituents; no other groups come under consideration here, since those containing nitroso or quinone groups already belong to the dye-stuffs.

In addition to sulphonation and nitration, the following operations are performed in the preparation of the various derivatives:—

1. Interchange of SO_3H and OH in the soda melt, or treatment with aqueous caustic alkalis.

In the amidosulpho acids of naphthalene, both the SO_3H and the NH_2 groups are replaced by OH through the action of alkalis, though, when this action is mild, sometimes only the first of these groups is so replaced. When several sulpho groups are present together, it is frequently possible to so regulate the fusion that only a partial displacement by hydroxyl groups ensues.

2. Elimination of SO_3H by heating with water or acids; this is particularly easy when the sulpho group is in the α -position.

3. Interchange of SO_3H and NO_2 by treatment with fuming nitric acid.

4. Reduction of NO_2 to NH_2 .

5. Replacing NO by OH, by diazotisation and boiling with water. Occasionally the displacement of the amido group by hydroxyl can be effected by heating with dilute acids, sulphurous acid in particular (Ger. Pat., 109,102, By.), or alkalis; sometimes even by simple heating with water, under pressure, the salts of α -naphthylamine, for example, being converted into α -naphthol by this treatment.

6. Displacing OH by NH_2 by heating with ammonia.

7. Migration of the SO_3H group, a phenomenon observed with special frequency in the naphthalene series. Thus,

for example, α -naphthylamine when heated with English sulphuric acid furnishes in succession 1. 4., 1. 5. and 1. 6. naphthylaminesulphonic acid.

The sulpho group can also migrate from a benzol nucleus into the naphthalene nucleus. Thus the heating of α -naphthylamine with sulphanilic acid gives (1) naphthylamine, (2) sulphonic acid.

For the investigation of the constitution of most of the compounds now in question we are indebted to the researches of Cleve, Armstrong, Wynne, Erdmann, and Dressell and Kothe, who have also determined the laws governing the entry of the sulpho and nitro groups.* With these laws we shall now proceed to deal.

The nitration of naphthalene furnishes α -nitronaph-

thalene, NO_2
, from which α -naphthylamine is obtained

by reduction. β -naphthylamine cannot be prepared in this manner, but is obtained by treating β -naphthol with ammonia, hydroxyl being here displaced by NH_2 . In the further nitration of α -nitronaphthalene, as also in nitrating the various naphthalene sulpho acids, the same tendency of the nitro group towards the α -position is observed; and it is only in a few cases that this entry also takes place in the β -position. Thus α -nitronaphthalene furnishes 1. 5. and 1. 8. dinitronaphthalene; and it may therefore be accepted as a rule that in comparison with a pre-existing NO_2 or SO_3H group in the α -position in the molecule, the newly introduced nitro group preferably assumes the position 1. 5. or 1. 8. With relation to an existing SO_3H group in the β -position, the newly introduced nitro group seeks the most remote α -position, or the meta α -position. In such cases the formation of the ortho derivative is never observed.

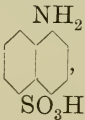
* See also P. Julius, *Chem. Zeit.*, 1894, pp. 180, 181.

According to the law discovered by Armstrong and Wynne, the SO_3H group in sulphonation takes up the α -position at low temperatures, but the β -position at high temperatures; and this applies also to the progress of further sulphonation. Furthermore, it is here found that at low temperatures the newly introduced SO_3H group takes up the most remote α -position, and at high temperatures the most remote β -position, but never the relative ortho, para or peri position with regard to an existing sulpho group. Exceptions to this rule, however, have recently been discovered by Dressel and Kothe.* The rule in the sulphonation of α -naphthylamine is that the sulpho group enters in 4. or 5., and if these be already occupied, seeks the positions 6. 7. or also 2.

According to the temperature employed, the sulphonation of naphthalene furnishes α - or β -naphthalenemonosulphonic acid, from which the corresponding valuable naphthols are obtained. As already mentioned, β -naphthol is also the material for the production of β -naphthylamine, whereas α -naphthylamine is formed by the nitration of naphthalene and by subsequent reduction.

By the sulphonation of β -naphthol we obtain two naphtholdisulphonic acids, the sodium salts of which play a great part—as salts R and G—in the production of “Ponceaus”.

For a more thorough account of these naphthalene derivatives the reader is referred to the literature cited in the final chapter. In the meantime the only one that need be

mentioned is the so-called “naphthionic acid,” , which

is obtained by the sulphonation of α -naphthylamine. This substance, as a component of the first of the benzidine dye-

* *Berl. Ber.*, vol. xxvii., pp. 1193, 2137.

stuffs, Congo Red, was apparently the cause of the impulse given to the highly fruitful researches after new naphthylamine and naphtholsulphonic acids.

The two phenylnaphthylamines are formed on heating the corresponding naphthols with aniline and aniline chloride. Phenyl α -naphthylamine can also be produced by heating aniline with α -naphthylamine chloride. Various tolylnaphthylamines can also be prepared in an analogous manner.

The dinaphthylamines corresponding to the diphenylamines can be recovered in the same way as these latter. One of them is formed in fair amount as a bye-product in the preparation of β -naphthylamine from β -naphthol and ammonia. By the action of concentrated hydrochloric acid, assisted by strong heat, it is converted into β -naphthol and β -naphthylamine.

Another interesting process is the production of β -dinaphthylamine and its derivatives by the action of sulphurous acid on β -naphthylamine and the derivatives thereof (Ger. Pat., 114,974).

Naphthidine, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 - \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$, *i.e.*, the naphthalene derivative corresponding to benzidine, has been prepared by Nietzki and Goll by reducing azonaphthalene to the corresponding hydrazo compound, and subjecting the latter to the benzidine transposition. It has not found any practical application.

The α - and β -oxynaphthoic acids, corresponding to salicylic acid, which are employed in the production of mordant dye-stuffs, can be obtained in a manner analogous to that usual in the preparation of salicylic acid.

The methods already described in connection with the benzol compounds have also rendered the aldehydes of the naphthalene series technically accessible.

Nitro- and nitrosonaphthols, as also dioxynaphthoqui-

none, are employed as dye-stuffs (see Nitro and Nitroso dyes, and Alizarine Black).

Apart from their uses in the manufacture of dye-stuffs, several of the naphthalene derivatives also find employment in medicine ; of these, asaprol is the lime salt, and alumnol the aluminium salt, of a β -naphtholsulphonic acid ; they are used as antiseptics. Thermine, which, in contrast to antipyretica, increases the bodily temperature, is tetrahydro β -naphthylamine.

In addition to the members of the fatty series (methyl chloride, etc.) long employed in the manufacture of dye-stuffs, others—phosgene and formaldehyde—have recently begun to play a part therein. The former of the two— COCl_2 —is formed by passing carbon monoxide and chlorine gas over animal charcoal, in presence of a cooling mixture, and serves in the production of triphenylmethane dye-stuffs. Formaldehyde — CH_2O —by reason of the smooth and almost quantitative course of its numerous reactions, is the most important of the aliphatic compounds for the manufacture of dye-stuffs. It is also largely used, under the name formalin (40 per cent. solution), as a disinfectant. The method of preparation consists in oxidising the vapours of methyl alcohol by atmospheric oxygen, in presence of an oxygen carrier or porous substances.

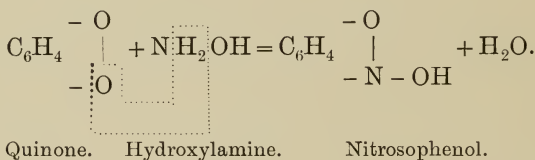
Lactic acid has latterly come into limited use as a solvent for dyes. It is prepared by heating saccharine materials with milk of lime under pressure.

THE ARTIFICIAL DYE-STUFFS (COAL-TAR DYES).

NITROSO DYE-STUFFS.

WHEN sulphurous acid is allowed to act on phenols, nitrosophenols, *e.g.*, $C_6H_5OH + HNO_2 = C_6H_4 \begin{smallmatrix} OH^{(1)} \\ NO_{(4)} \end{smallmatrix} + H_2O$, are formed.

According, however, to H. Goldschmied, the same nitrosophenol is obtained by the action of hydroxylamine on quinone. To explain its method of formation by this reaction, one is compelled to ascribe to nitrosophenol another constitutional formula, as will be evident from the following equation :—

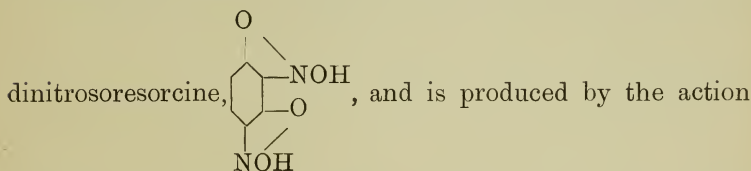


Nitroso bodies credited with a constitution of this kind are termed oximes, and it is, indeed, very probable that all the nitroso dye-stuffs are oximes ; consequently their chromophorous group would be $\begin{array}{c} - O \\ | \\ - NOH \end{array}$.

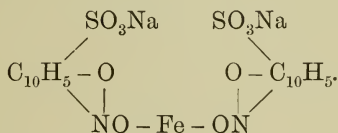
The nitroso dye-stuffs are of recent discovery, following upon the observation that o. nitrosophenols furnish with iron salts stable green compounds, and brown compounds with chromium salts. They are few in number, of acid

character, polygenetic, and distinguished by a special affinity for iron. Their iron lakes are green, the chrome lakes brown, both being particularly fast towards light and washing. The practical application of these dyes, however, is a very limited one, since only their iron lakes are of value, and the colour even of these is deficient in brightness. They are best adapted for use in calico printing.

Resorcine Green (Alsatian Green, Solid Green O) is



of sulphurous acid on resorcine. **Naphthol Green B** (Casella) is produced by acting with iron salts on nitroso β -naphthol-sulphonic acid, and is credited with the following constitution:—



Applied to wool and fixed as an iron lake, Naphthol Green gives a green that is fast to light. It is unsuitable for dyeing cotton.

Dioxine (L.) 1. nitroso- 2. 7.-dioxynaphthalene behaves like Naphthol Green.

Gambines (R. H. and Act.) are nitroso dye-stuffs from α - and β -naphthol and 2. 7. dioxynaphthalene.

To this group also belongs Milling Green S (L.).

NITRO DYE-STUFFS.

The nitro dye-stuffs all contain the chromophorous group "NO₂". According to Armstrong, however, this cannot be the sole cause of the coloration, colourless nitro bodies being also known. This worker ascribes to the colourless p. nitrophenol the general constitution of the nitro bodies, OH.C₆H₄-N $\begin{smallmatrix} \text{O} \\ \text{=} \\ \text{O} \end{smallmatrix}$, but to the coloured o. nitrophenol the

constitution $\text{O}=\text{C}_6\text{H}_4=\text{N}\begin{smallmatrix} \text{O} \\ \text{=} \\ \text{O} \end{smallmatrix}$.

The majority of the nitro dye-stuffs contain hydroxyl groups. They are all acid, and nearly all exhibit the properties common to aromatic nitro bodies in general, such as the explosive character of the salts, the bitter flavour, and the more or less pure yellow colour. The majority are also poisonous. They belong to the older artificial dyes, and, thanks to their easy application, high equalising property and pure yellow colour, were very largely employed for dyeing silk and wool, especially in the early days of the coal-tar dye industry. Their fugitive character, however, has led in recent times to their supersession for the most part by the azo dyes. They can all be dyed in a bath slightly acidified with sulphuric acid, in wooden vessels (copper spoils the purity of the colour), but are unsuitable for dyeing cotton.

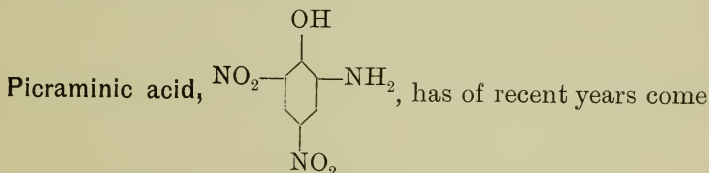
At present Naphthol Yellow S is the only dye-stuff of this class of any importance in the dyeing of textile fibres.

Picric acid, $\text{C}_6\text{H}_2\begin{smallmatrix} \text{NO}_2^{(2)} \\ \text{NO}_2^{(4)} \\ \text{NO}_2^{(6)} \end{smallmatrix}$, is the oldest artificial organic

dye-stuff, its formation by the action of nitric acid on indigo having been observed by Woulfe as long ago as 1771. It is prepared either by the direct nitration of phenol, whereby o. and p. mononitrophenol are first formed, or in a more

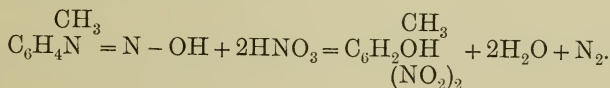
productive manner by treating phenolsulphonic acid with concentrated nitric acid. Picric acid is not itself explosive, though its salts exhibit this property in a high degree, and are employed in the manufacture of melinite for charging shell.

Picric acid was formerly largely used for dyeing wool and silk yellow, as also for toning greens and reds; but at the present time is no longer employed for this purpose, its dyeings being very fugitive to washing, though pure in colour (yellow with greenish tinge). On exposure to light the colour turns somewhat orange, but does not readily fade. It is turned brown by alkalis.



into extensive use as a component for the manufacture of azo dye-stuffs.

Victoria Orange, or saffron substitute, $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3\text{ONa}$, is a variable mixture of the sodium salts of o. and p. dinitrocresol, and is prepared either by treating cresolsulphonic acid with concentrated nitric acid, or by diazotising a mixture of o. and p. toluidine and treating the resulting diazo compounds with nitric acid:

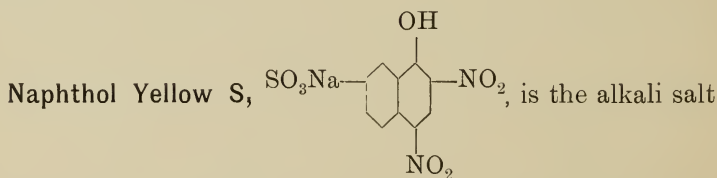


This dye-stuff is yellow to orange in colour, but is too fugitive to be used in dyeing textiles. It is, however, employed for colouring delicacies (liqueurs, maccaroni, etc.), though this should be prohibited by reason of its extremely—and indeed fatally—poisonous character. Victoria Orange

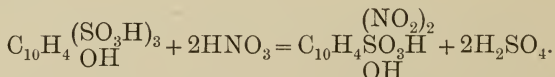
can be readily sublimed, a peculiarity capable of application as a qualitative test for its presence, by placing the suspected sample between filter paper and heating it to about 100°C . If this dye be present the paper will be stained yellow. Martius Yellow also behaves similarly in this respect. The potassium salt of dinitro-orthocresol has been introduced by Fr. Bayer & Co., under the name antinonnin, as a remedy against fungoid growths on wood, masonry, etc.

Ammonia salts of nitro cresols are used as explosives. Thus the ammonia salt of trinitro cresol is the chief constituent of the Austrian explosive ecrasite, and probably also of the French cresylite.

Martius Yellow, $\text{C}_{10}\text{H}_5(\text{NO}_2)_2\text{ONa}^{(\alpha)}$, is the sodium (more rarely potassium) salt of 2.4. dinitro α -naphthol. It was the first really handsome artificial yellow dye prepared by the synthetic process (Martius, 1864), and is produced either by direct nitration of α -naphthol, or by boiling diazotised α -naphthylamine with nitric acid. This dye-stuff is also used for colouring delicacies, but its poisonous nature renders it unsuitable for this purpose. Like Victoria Orange, it readily sublimes, and can therefore be tested for qualitatively by this means.



of the monosulphonic acid of Martius Yellow. It is prepared by treating naphthol di- or trisulphonic acid with nitric acid :



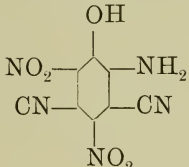
Naphthol Yellow is much faster than the other nitro

dye-stuffs, and is frequently used in dyeing animal textile fibres, either alone in the production of pure yellow shades, or for mixed colours, such as green, etc.

The following nitro dye-stuffs have never attained any practical importance, and are no longer used in dyeing textile fibres.

Phenyl Brown is impure dinitrophenol.

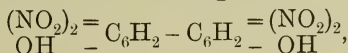
Picrocyaminic acid or isopurpuric acid is prepared by heating picric acid with potassium cyanide; according to

Nietzki, it has the formula . The ammonia

salt was formerly sold under the name of "Grenat soluble" (soluble garnet).

Salicyl Yellow is a mixture of several dye-stuffs prepared by the action of nitric acid on monobromosalicylic acid. It gives very handsome dyeings, which, however, are expensive and are very fugitive to light.

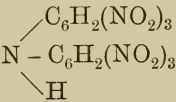
Palatine Orange is tetranitrodiphenol,



and results from the action of nitric acid on diphenol. It is used for staining paper, and is more stable than most other nitro dye-stuffs.

Aurotine is tetranitrophenolphthalein.

Sun Gold (tetranitronaphthol) imparts very handsome, but equally fugitive, colours to wool and silk.

Aurantia is hexanitrodiphenylamine, , and

is formed by nitrating diphenylamine. It produces a very fine orange colour, but is no longer in use, since it gives rise to eruptions on contact with the skin.

The class of nitro dye-stuffs can further be enlarged by a series of products that have recently been prepared by nitrating dyes belonging to other groups. Thus, the treatment of the azo dye-stuff Orange IV. (*q.v.*) gives several nitro bodies, put on the market under the names: Azo Yellow, Azoflavine S, Indian Yellow, Citronine. The nitration of alizarine furnishes Alizarine Orange.

The Soc. Anon. des Mat. Col. St. Denis has also patented several nitro dye-stuffs obtained by nitrating Fuch-sine and Methyl Violet, but has not yet placed them on the market. They are, however, of no value as dye-stuffs.

AZO DYE-STUFFS.

All substances which are constituted according to the type $C_6H_5N=N-C_6H_5$ are termed azo bodies. They therefore contain the $-N=N-$ group, the two free valences of which are combined with aromatic nuclei. The phenyl groups can be replaced by a large number of other groups, such as tolyl, xylyl, naphthyl, etc., from which it is very evident that the number of possible azo bodies must be considerable.

All the azo bodies built on the above type are coloured, but are not dye-stuffs; however, thanks to the chromophorous group $-N=N-$, they are chromogenes, and are converted into dye-stuffs on the introduction into their molecule of the auxochrome groups, such as OH or NH_2 . Thus, for example, azobenzol, $C_6H_5-N=N-C_6H_5$, is not a dye-stuff, though red in colour; whereas, on the one hand, oxyazobenzol, $C_6H_5N=N-C_6H_4OH$, and amidoazobenzol, $C_6H_5-N=N-C_6H_4NH_2$, are dye-stuffs.

The azo dye-stuffs also belong in part to other groups, in so far as they contain other chromophorous groups in addition to the azo group.

They are, almost without exception, produced by converting a primary amine into the corresponding diazo body by the action of nitrous acid, and then allowing phenols, amines or their derivatives to react on the product (Griess' reaction).

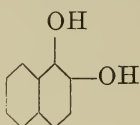
Not all the primary aromatic amines are susceptible of diazotisation with nitrous acid, and of forming azo dye-stuffs when coupled with other components. Thus Marckwald * found that, of three amidopyridines, only the β -derivative could be readily diazotised. Furthermore, amido groups in the ortho position with regard to an azo group, are for the most part insusceptible of diazotisation. In coupling diazo bodies with phenols and amines, it appears to be a law that the diazo group enters the para position with regard to any OH or NH_2 group present. Should this position be already occupied, it takes the ortho position; if this latter also is occupied, either the group in the para position is displaced by the diazo group, or—which is usually the case—no azo dye-stuff is formed at all. When phenols are coupled with diazo bodies in a caustic alkali solution, there results, when possible, in addition to para, mostly orthoazo dye-stuffs; furthermore—by double entrance of the diazo group—tetrazo dye-stuffs as well.

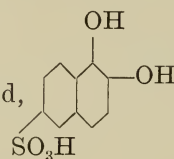
It has also been found that the reaction of diamido- and dioxybenzols on diazo bodies produces azo dye-stuffs solely when the first-named belong to the meta series. Hence only the metadiamido- and metadioxybenzols are capable of furnishing azo bodies with diazo compounds. Ortho- and paradiamido- and dioxybenzols react in another manner. This uniformity has been named the chrysoidine law, after the chrysoidine prepared by the action of meta-phenylenediamine on diazobenzol.

* *Berl. Ber.*, 1898, p. 2496.

This law only applies when the process is carried out in the usual manner (see below). Witt and Johnson, however, have shown that under certain conditions ortho and para derivatives can also furnish azo dye-stuffs with diazo compounds, *e.g.*, pyrocatechin and hydroquinone (the latter used as monobenzoate).

In the naphthalene series the conditions are quite different. In the first place, the chrysoidine law does not apply here,

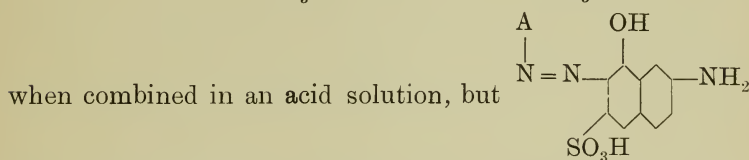
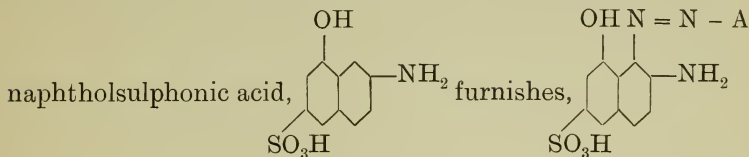
since both β -naphthohydroquinone, , and its

sulpho acid, , furnish azo dye-stuffs with diazo compounds.

The rules followed by the coupling process here are usually as follows: α -naphthol and α -naphthylamine give para-azo dye-stuffs when acted on by diazo compounds; but orthoazo dye-stuffs are formed when a sulpho group stands in the ortho or in the peri position with relation to a free para position. The orthoazo dyes are more valuable as such; but if the amidoazo bodies are to be further diazotised and coupled, only the para-azo members can be used, the amido groups in the others being for the most part non-diazotisable. By reason of the two relatively para-azo groups, such "tetrazo dye-stuffs" have a certain similarity with the benzidine dye-stuffs to be described later, inasmuch as, without being direct substantive dyes, they nevertheless exhibit the good properties of the latter in the dyeing of wool.

Divergent dye-stuffs are furnished by some of the amido-naphthol sulphonic acids, according as their conjunction with a diazo compound is effected in an acid or an alkaline solution,

since in one case the OH group, in the other the NH_2 group, has an action of "orientation". Thus, for example, γ -amido-



in an alkaline solution, A representing an aromatic nucleus.

Diamido-, dioxy-, oxyamidonaphthalenes and their sulpho acids behave in the following manner during the coupling process: Naphthylenediamines behave like the corresponding dioxynaphthalenes; 1. 8. diamido- or dioxynaphthalene gives para-azo dye-stuffs; 2. 6. and 2. 7. diamido- or dioxynaphthalene gives para-azo dye-stuffs in alkaline solutions, but orthoazo dye-stuffs in acid solutions. With the 1. 8. diamido- or dioxynaphthalene-4.-sulphonic acid the azo group enters 7., but in 1. 8. diamido- or dioxynaphthalene-3. 6.-disulphonic acid it enters 2. or 7. The conditions are highly diversified in the case of the amidonaphthol sulphonic acid. Bülow* divides them into several classes.

1. Such as are either insusceptible of being coupled at all, or, if so, only under special conditions. To these belong sulpho acids of the 1. 2. and 2. 1. amidonaphthols.

2. Such as are readily coupled under all conditions, and invariably furnish the same product; *e.g.*, 1. 8. amidonaphthol-5. 7.-disulphonic acid.

3. Such as furnish orthoamidoazo compounds in acid solution, and orthoxyazo dye-stuffs in alkaline solution, *e.g.*, 1. 8. amidonaphthol-3. 6.-disulphonic acid (H-acid), 2. 8.

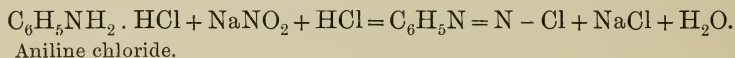
* *Chem. Ztg.*, **19**, p. 1011.

amidonaphthol-6.-sulphonic acid (γ -acid), and 2. 5. amidonaphthol-7.-sulphonic acid (J-acid). Some of them, *e.g.*, 1. 8. amidonaphthol-4. and 5.-sulpho acids, furnish tetraazo dye-stuffs in alkaline solution.

The general principles of the formation of azo dye-stuffs may be enunciated as follows :—

(a) From phenols.

The aqueous solution of the salt of a primary amine is first treated with sodium nitrate and hydrochloric acid, in presence of a refrigerating mixture whereby a diazo compound is formed, *e.g.* :—



The resulting diazobenzol chloride is next coupled with the phenol by allowing the solution of the former to run gradually into the alkaline solution of the phenol, *e.g.* :—



It is necessary to see that the solution remains alkaline throughout, the formation of the dye-stuff being retarded by the presence of free mineral acids.

When the dissolved diazo compound has been mixed with the phenol, the whole is left for the reaction to attain completion. In some cases the dye-stuff settles down as a sparingly soluble alkali compound ; in others it remains in solution, and can be recovered as a salt by precipitation with sodium chloride, or in the free state by the aid of an acid.

(b) From amines.

The principle of the method is the same, except that the combination of the diazo compound with the dissolved amine is effected in a neutral or faintly acid solution. If the amine is difficult to dissolve in dilute acid, as is the case with some of the amidosulpho acids, the following method of diazotisation is employed.

The solutions of the nitrate and the alkaline salt of the amido acid are united, and the mixture is poured into hydrochloric acid or *vice versa*.

Naphthylamines and their sulpho acids, as well as dioxy-, diamido- and amido-oxynaphthalenes, are combined with the diazo compound in an acetic or weak hydrochloric solution, for the production of simple azo dye-stuffs.

In the formation of azo dye-stuffs the reaction generally proceeds very smoothly, the yield being quantitative, and, therefore, the components must usually be employed in the molecular proportions expressed by the equation of the reaction. When amines have to be diazotised, they must be well cooled with ice on account of the great instability of the resulting diazo compounds; with the sulpho acid of the amines, however, this precaution is not always necessary.

Moreover, the stability of the diazo compounds varies considerably. For instance, diazosulphanilic acid and diazonaphthionic acid are fairly stable; but care must be exercised in drying them, on account of their explosive character. The diazo compound of o. anisidine is particularly stable, since it can be heated even up to 100° C., without undergoing decomposition.* Of late, "stable diazo compounds," that can be stored in the solid state, have been prepared by various methods; they are employed in the production of azo dyes on the fibre (Nitraniline Red, Nitrosamine, and the "Ice colours").

According to patents taken out by the Höchst Farbwerke, stable diazo compounds can be obtained by evaporating their strongly acid solutions at 45° C., and mixing them with incombustible materials; or the diazo solution is brought into the solid state by an addition of anhydrous aluminium sulphate. L. Cassella & Co. diazotise in a concentrated sulphuric solution, and mix with sufficient anhydrous sodium

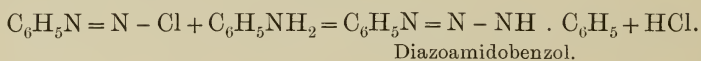
* Gattermann, *Berl. Ber.*, 1899, p. 1136.

sulphate to form bisulphate. Finally, diazo compounds of a highly stable character are prepared with salts of naphthalene, or naphtholsulphonic acids (*Soc. Prod. Chim. Thann & Becker*).

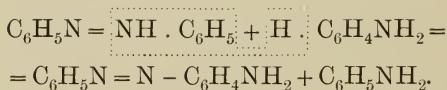
For some hitherto undiscovered reason the coupling of diazo compounds with phenols is sometimes effected with difficulty, and under other circumstances than those described above.

In some instances the reaction between diazo compounds and the amines and phenols proceeds in quite an abnormal manner. These deviations from the general law will now be described:—

1. When aniline is allowed to react on diazobenzol chloride, the resulting product is not amidoazobenzol, as might be anticipated, but a compound to which is given the name of diazoamidobenzol:

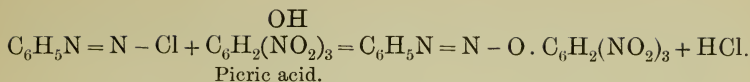


The same behaviour is exhibited by o. toluidine, and by m. and p. xylydine. On heating this diazoamido compound, in the dry state, to 40° C., with aniline and a little aniline chloride, it is converted into amidoazobenzol. According to Kékulé, the reaction may be expressed as follows:—



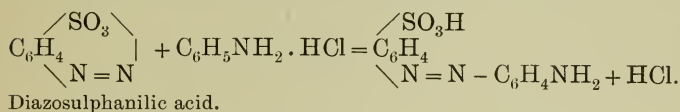
The formation of diazoamido compounds during the diazotisation of amines can be entirely prevented by using a faintly acidified solution of nitrite.

2. Phenols of a strongly acid character, such as picric acid or p. nitrophenol, when allowed to act on diazo compounds, furnish, instead of azo compounds, salts that can be classed along with diazoamido compounds:—

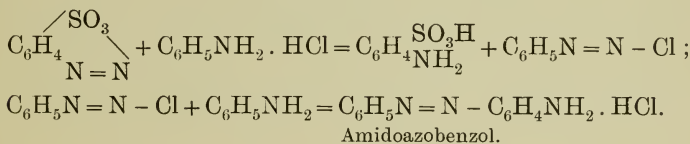


(Normally the product should be $\text{C}_6\text{H}_5\text{N}=\text{N}-\text{C}_6\text{H}(\text{OH})(\text{NO}_2)_3$.)

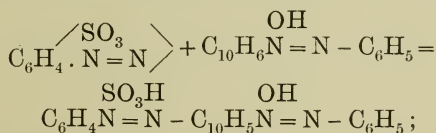
3. If diazosulphanilic salts be allowed to act on aniline chloride the process goes on normally to a small extent, amidoazobenzolsulphonic acid being formed :—



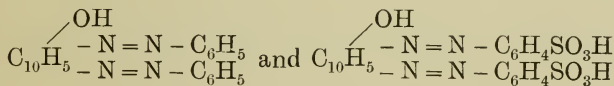
However, in addition, there occurs a peculiar atomic displacement, an exchange of the diazo group with the amido group, and amidoazobenzol is formed :—



In the reaction of diazosulphanilic acid on benzoazo α -naphthol the process should normally go on as follows :—

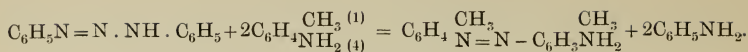


whereas, as a matter of fact, the following compounds are formed :—

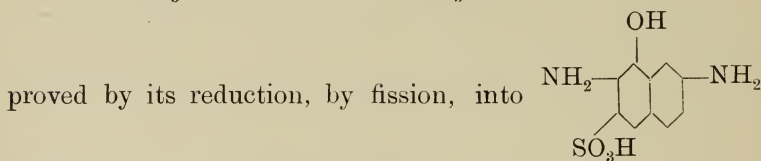
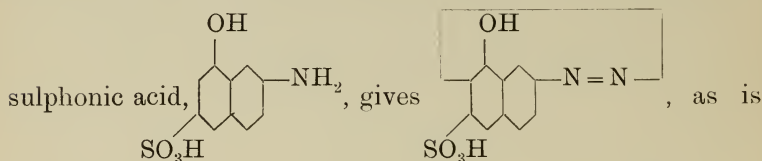


Diazobenzoic acid 1. 3. behaves in this respect exactly similar to diazosulphanilic acid.

Abnormalities may also occur in the transposition of the diazoamido compounds, *e.g.* :—

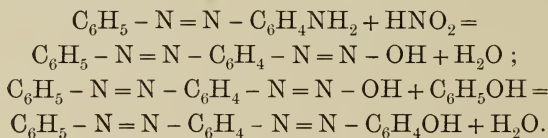


Finally, it should be mentioned that the diazo compounds of certain amidonaphtholsulphonic acids undergo a kind of auto-coupling when treated with alkalis, *e.g.*, γ -amidonaphthol-



(M. L. Br.; Ger. Pat., 92,012).

If an azo compound contain a free amido group, it can be diazotised in the same way as a simple amine; and if a phenol or amine be allowed to act on the resulting compound, a tetrazo or diazo compound is formed:—



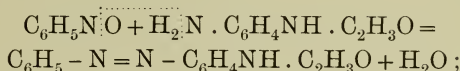
A product of this kind, obtained by double diazotisation, is termed a secondary diazo or tetrazo compound; those obtained by the entry of two diazo groups into a single component are named primary diazo or tetrazo dye-stuffs. In the preparation of secondary diazo dye-stuffs it is usually the practice to filter and press the (insoluble) diazo compound of the amidoazo compound, in order to remove the excess of the nitrite and the second component, after which the third component is brought into reaction.

Azo compounds containing three $-\text{N}=\text{N}-$ groups are termed trisazo bodies.

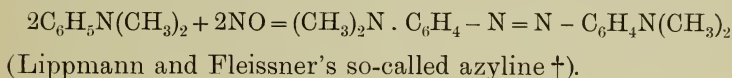
OTHER METHODS OF PRODUCING AZO COMPOUNDS.

According to W. Lob,* azo compounds unattainable by the above-described general reaction (Griess' reaction), can be prepared by the electrolysis of two nitro compounds, or of a nitro and an amido compound.

Azo compounds also result from nitroso compounds and hydrazines (with elimination of nitrogen); from nitroso compounds and amines, *e.g.* :—



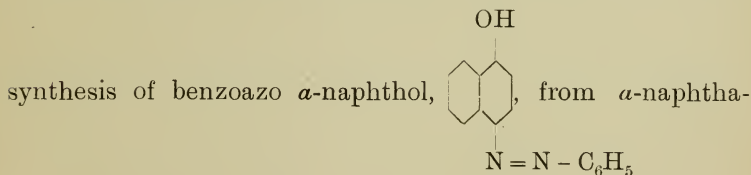
finally also from the action of NO on dialkylaniline :—



CONSTITUTION OF THE AZO DYE-STUFFS.

So far as the constitution of the azo dye-stuffs is concerned, this is by no means so accurately defined as one might be inclined to suppose from the foregoing particulars. Well-founded doubts have arisen of late as to whether all the oxyazo compounds are really azo compounds, or whether some of them should not rather be regarded as hydrazones, *i.e.*, derivatives of phenylhydrazine.

The incentive hereto was given by Zincke ‡ through his

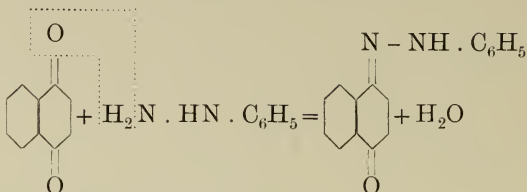


* *Berl. Ber.*, 1898, p. 2201; see also K. Elbs, *Zeits. Angew. Chem.*, 1899, p. 389.

† *M. f. Ch.*, 1882, pp. 705-714.

‡ *Berl. Ber.*, 17, p. 3026.

quinone and phenylhydrazine, according to which this compound should be regarded as a hydrazone :



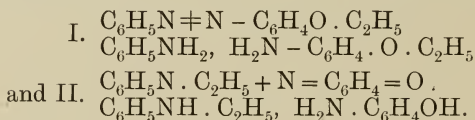
α -Naphthaquinone. Phenylhydrazine.

For many oxyazo compounds, especially those ensuing from β -naphthol, the hydrazone formula gives a better explanation of their peculiar behaviour than the azo formula ; others, however, behave as might be expected from oxyazo compounds. If we compare these formulæ, *e.g.*, in the case of oxyazobenzol :



it becomes evident that they differ in respect of the position of the motile hydrogen atom, this being in the first case combined with oxygen as hydroxyl hydrogen, and in the other combined with nitrogen as imide.

It might be supposed that this question could be readily solved by dissociating an ether of the oxyazobenzol with reducing agents, and examining the resulting product :—



In the former case—as the above formulæ clearly show—phenetidine should be obtained as well as aniline ; whilst in the second we should obtain amidophenol and ethylaniline.

Similar experiments have actually been made by a number of investigators. H. Goldschmidt* obtained from ortho-

* *Berl. Ber.*, **24**, 2300, 1324.

oxyazo compounds acetyl and benzoyl derivatives containing the acid radicle on the nitrogen, whereas, on the other hand, Weinberg* has shown in the case of an ortho-oxyazo compound that an acetylation of the hydroxyl group occurs. Some workers assume the ortho-oxyazo compounds to be differently constituted to the para derivatives, the former being hydrazones—according to Goldschmidt, K. Auwers,† and McPherson‡—and the latter oxyazo compounds; whilst, on the other hand, R. Möhlau and E. Kegel§ regard the paraoxyazo bodies as hydrazones. These divergent opinions permit the conclusion that we have here to do with tautometry; that consequently in the ortho- and the paraoxyazo compounds both the hydrazone form and the azo form are capable of existence. The question has finally been decided by A. Hantzsch,|| according to whose researches both the ortho- and the paraoxyazo compounds are hydrazones in their free state, whereas their salts are true oxyazobenzol derivatives.

Opinions on the constitution of the diazo compounds have also latterly undergone alteration. Whereas formerly the sole formula applied to diazobenzol was $C_6H_5 - N = N - X$, wherein X represented an acid radicle, OH, or a monovalent metal, one is now constrained to assume that the diazo compounds can exist in different forms. For the elucidation of this complicated relation we are chiefly indebted to the researches of E. Bamberger and A. Hantzsch.

Bamberger assumes structural differences, whilst Hantzsch explains the divergent behaviour of the diazo bodies by the assumption of stereoisomerism. Both workers accept the formula proposed by Blomstrand for diazobenzol chloride, $C_6H_5 - N - Cl$
 $\begin{array}{c} || \\ N \end{array}$; and diazo compounds constituted in this

* *Berl. Ber.*, **20**, 3171.

† *Ibid.*, **29**, 2361.

‡ *Ibid.*, **28**, 2414.

§ *Ibid.*, **33**, 2358.

|| *Ibid.*, **32**, 3089.

manner have been named phenylazonium compounds, or normal diazo compounds. Bamber ascribes the formula $C_6H_5 - N = N - OMe$ to the metallic compounds, and calls them isodiazo compounds, whilst Hantzsch expresses them by $C_6H_5 - N$
 $MeO \cdot N$, and names them syndiazo compounds. The

differences between the two series disappear on their transposition into an azo compound.

The third form, resulting from the action of alkalis on diazo compounds and first discovered by C. Schraube and C. Schmidt,* does not show the known capacity for reaction exhibited by the diazo compounds, and does not give any azo compound with phenols. It has been named the inactive phenylnitrosamine form by Bamberger, $C_6H_5NH \cdot NO$, or $C_6H_5N \cdot Me \cdot NO$, and is regarded by Hantzsch as an anti-

diazo compound, $C_6H_5 - N$
 NOH , or $C_6H_5 - N$
 $NOMe$. By the action

of acids (even CO_2) this inactive form is easily converted into the diazo form that can be coupled with phenols (see Nitrosamine).

The era of the azo dye-stuffs commences with the year 1876 and the introduction into practice of the chrysoidine discovered by Caro and Witt. True, a few of them were known before, but the method of preparation was too troublesome, it being at that time considered necessary to isolate the diazo compound before combining it with the phenol or amine. At the present time the preparation of most of the azo dyes is one of the easiest and simplest operations known in chemical practice.

The azo dye-stuffs are of immense importance, and their number exceeds that of any other class of dye-stuffs by a

* *Berl. Ber.*, **27**, 514.

considerable amount. Many hundreds of azo dyes are known in commerce, and the number of those described in the literature of the Patent Office, without having attained any practical importance, is legion. Most of them are of an acid nature—sulpho acids. The number of the basic azo dyes is limited. The simple bodies are yellow to orange in colour; but by piling up groups in the molecule the colour is gradually changed into red, blue, brown and black. A remarkable feature is the lack of green dye-stuffs of this class, and it is only of late that a few have been prepared. The number of yellows with a greenish tinge is also very small.

To facilitate the study of the azo dye-stuffs we will consider them in groups, those belonging to the same group and having a similar constitution behaving alike as dye-stuffs.

BASIC AZO DYE-STUFFS.

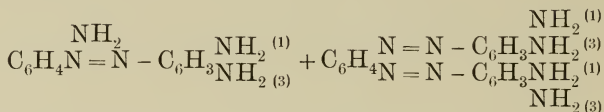
Aniline Yellow, $C_6H_5N=N-C_6H_4NH_2$ (amidoazobenzol), was the first of the azo dye-stuffs made. It is a beautiful yellow, but on account of its fugitive character has not found employment for dyeing, and its importance consists in the fact that it forms the raw material for the production of numerous other dye-stuffs.

Butter Yellow is the dimethyl derivative of Aniline Yellow, and is employed to measure the affinity of acids and bases by the optical method of W. Lellmann.

Chrysoidine, $C_6H_5N=N-C_6H_3\begin{smallmatrix} NH_2^{(1)} \\ NH_2^{(3)} \end{smallmatrix}$, is formed by the action of m. phenyldiamine on diazobenzol chloride. It was discovered and introduced into practical application by Caro and Witt, is used in cotton dyeing and printing for the production of chamois brown and for tinting, and also serves for dyeing leather, fats, etc. Light shades can be produced

direct, *i.e.*, on cotton without the intervention of a tannin bath. All these colours are bright but fugitive, and they will not stand steaming. Chrysoidine is largely sold in the condition of mixtures, *e.g.*, with Fuchsine as Cardinal, with Safranine as Scarlet for cotton, etc.

Vesuvine, Bismarck Brown, Manchester Brown, is a mixture of



and is produced by the action of nitrous acid on m. phenylene-diamine. Its uses and dyeing properties are analogous to those of Chrysoidine.

According to E. Täuber and Fr. Walder, commercial Bismarck Brown contains as its principal constituent the diazo compound occupying the second place in the foregoing equation.

A number of new basic azo dye-stuffs are produced from dimethyl-p.-amidobenzylamine, $(\text{CH}_3)_2\text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{NH}_2$. Benzyldimethylamine, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{N}(\text{CH}_3)_2$, is first nitrated, then reduced, the resulting amido group being then diazotised and coupled with phenols. To this class belong **New Phos-**

phine G (C.), $(\text{CH}_3)_2\text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 - \text{N}=\text{N} - \text{C}_6\text{H}_3\overset{\text{OH}}{\underset{\text{OH}}{\text{N}}}^{(1)}$, from dimethylamidobenzylamine and resorcine; and **Tannin Orange (C.)**, $(\text{CH}_3)_2\text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 - \text{N}=\text{N} - \text{C}_{10}\text{H}_6\text{OH}(\beta)$, from the same base and β -naphthol.

To the same class also belong the so-called **Janus dyes** of the Hoechst Farbwerke, which are derived from amido-benzylamines and from p. and m. phenyldiamine. They are secondary tetrazo dye-stuffs from amidoammonium bases, *e.g.*, from amidophenyltrimethylammonium,



Janus Red (M. L. Br.) is one of them. This is produced by diazotising the aforesaid base, coupling with *m.* toluidine, diazotising again, and combining with β -naphthol. The formula is therefore:—



Azophosphine (M. L. Br.) is obtained by coupling diazotised amidophenyltrimethylammonium with resorcine.

Janus Green and **Janus Blue** are safranine azo dye-stuffs (*q.v.*).

These dye-stuffs are principally employed in dyeing semi-woollens. They dye cotton direct, but, unlike other substantive dyes, in an acid bath.

Finally it may be stated that basic azo dye-stuffs may be prepared by treating oxyazo dye-stuffs with formaldehyde in the presence of a secondary fatty amine. The group

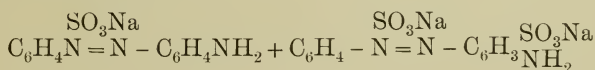
$-\text{CH}_2 \cdot \text{N} \begin{array}{c} -\text{R} \\ -\text{R}_1 \end{array}$ enters the dye-stuff and imparts a basic character thereto (Ger. Pat., 95,546 (By.)).

SIMPLE ACID AZO DYE-STUFFS

(MOSTLY OXYAZO COMPOUNDS OR THEIR SULPHO ACIDS).

Soudan G, $\text{C}_6\text{H}_5\text{N} = \text{N} - \text{C}_6\text{H}_3 \begin{array}{c} \text{OH}^{(1)} \\ \text{OH}_{(3)} \end{array}$, is a yellow-brown dye-stuff, employed to colour varnishes, but not for dyeing textiles.

Fast Yellow is a mixture of amidoazobenzolmono- and disulphonate of soda:—



This is the most stable towards light of any of the yellow acid dyes, and also equalises very well. It is used in wool dyeing, for shading and the production of mixed colours;

and is also of some importance as a raw material for the preparation of tetrazo dye-stuffs.

A number of dye-stuffs in this group are derived from sulphanilic acid.

Chrysoine, or **Tropeoline O**, $\text{C}_6\text{H}_4\text{N}=\text{N}-\overset{\text{SO}_3\text{Na}}{\text{C}_6\text{H}_3}\overset{\text{OH}^{(1)}}{\text{OH}^{(3)}}$, is a handsome yellow of some interest in silk dyeing.

Orange I., **Tropeoline 000 No. 1**, α -Naphthol Orange, $\text{C}_6\text{H}_4-\overset{\text{SO}_3\text{Na}}{\text{N}=\text{N}}-\text{C}_{10}\text{H}_6(\text{OH})\alpha$, is very little used. **Orange II.**, **Tropeoline 000 No. 2**, β -Naphthol Orange (Roussin),

$\text{C}_6\text{H}_4-\overset{\text{SO}_3\text{Na}}{\text{N}=\text{N}}-\text{C}_{10}\text{H}_6\text{OH}(\beta)$, is a handsome dye-stuff, highly prized for dyeing wool and silk, and is, in fact, the most frequently used of all orange dyes. It is not very poisonous.

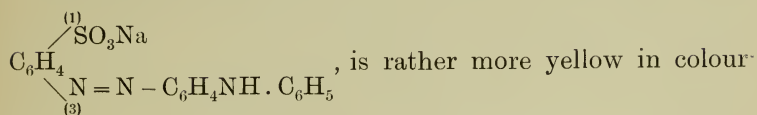
Orange IV., **Tropeoline 00**, **New Yellow**, $\text{C}_6\text{H}_4-\overset{\text{SO}_3\text{Na}}{\text{N}=\text{N}}-\text{C}_6\text{H}_4\text{NH}\cdot\text{C}_6\text{H}_5$, is largely used in wool dyeing, notwithstanding that it is turned red by acids.

The action of concentrated nitric acid on this dye-stuff furnishes variable mixtures of nitrated **Orange IV.**, which are put on the market as **Azo Yellow**, **acid Azo Yellow**, **Azoflavine**, **Indian Yellow**, **Citronine**, etc., and are of great importance in wool dyeing on account of their fastness towards acids. These dye-stuffs represent a successful combination of the advantages of the nitro and azo dye-stuffs.

Methyl Orange (**Orange III.**, **Tropeoline D**, **Helianthine**), $\text{C}_6\text{H}_4-\overset{\text{SO}_3\text{Na}}{\text{N}=\text{N}}-\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$. The only use of this dye-stuff is as an indicator in volumetric analysis, on account of its sensitivity towards acids. For this purpose it exhibits the advantage of not being altered by carbon dioxide or semi-combined sulphurous acid (thus differing from phenolphthaleine). Consequently it can be used for titrating carbonates

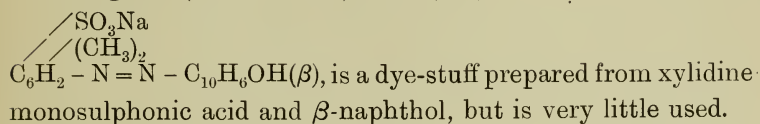
and for the determination of the free sulphuric acid in bisulphite.

Metaniline Yellow (Victoria Yellow (M. L. Br.)),



than its isomer Orange IV., and is used in wool dyeing, notwithstanding its poisonous nature, its chief employment, however, being in paper staining, carpet printing and colouring varnishes.

Orange R (B. A. S. F.), RR (Bi.),



These dye-stuffs were of importance as a new departure in the coal-tar dye industry, since they demonstrated the great value of the dye-stuff acids. The experience gained in this connection was transferred to other classes of dyes, the result being the production of the acid dye-stuffs of the triphenylmethane series and the alizarine group.

Whereas the acid azo dye-stuffs considered hitherto are produced almost without exception by the combination of a phenol with the diazo compound of a sulphonated amine, there are numerous others that can be obtained by combining a phenolsulphonic acid with a diazotised amine or the sulpho acid of same. In the one case therefore only the one component contains one or more sulpho groups; in the other these are present in both components. Some of these dye-stuffs are isomeric with members of the groups described above, from which, however, they differ in the more or less pure red colour they produce on wool and silk.

They belong to the most important of the dye-stuffs, and

are consumed in enormous quantities, especially in wool dyeing, for the production of imitation cochineal and for Bordeaux red.

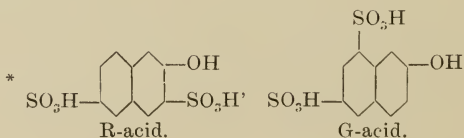
As an example of those prepared by combining a diazotised amine with a phenolsulphonic acid may be cited the **Ponceau (poppy) reds**, first introduced by the Hoechst Farbwerke. These are obtained from the isomeric xylidines by diazotising these bases and allowing them to react on the sodium salts of the two β -naphtholdisulphonic acids G and R* in alkaline solution. The general formula of these dye-stuffs is:—



Xylidine can be also replaced by cumidine, and the β -naphtholsulphonic acid R by one of the other naphthol-sulphonic acids.

The discovery of the Ponceau dyes (1878) was a matter of epoch-making importance for both the colour and the dyeing industries. They showed the way for the preparation of the first scarlet dyes and a number of similar products, all of which are remarkable for beauty and cheapness. At the same time the knowledge thus acquired with regard to the different behaviour of the above-named G and R salts, here used for the first time, had a highly stimulating influence on the subsequent synthetical preparation of dye-stuffs.

The salt G, for example, gives a yellow dye with benzol derivatives and a red with those of naphthalene. Their divergent behaviour revealed for the first time the important influence of the position of the sulpho groups on the character of the dye-stuff.



By varying the reaction employed in producing the Ponceau dyes, it was soon found possible to prepare a large number of new dye-stuffs, which are put on the market under different names—the scarlets as Ponceaus, Scarlet, etc., the brownish or bluish reds as Fast Red, Bordeaux, Archil Substitute, etc.

A few of these will be described in greater detail in the following lines :—

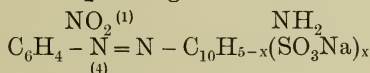
Orange G, $C_6H_5N=N-N-C_{10}H_4(OH)(SO_3Na)_2$, from aniline and G salt, is largely used for wool.

Palatine Scarlet (B.), **Cochineal Scarlet PS (By.)**, **Brilliant Cochineal (C.)**, $C_6H_3N=N-C_{10}H_4(OH)(SO_3Na)_2$, from m. xyldine and α -naphthol-3, 6.-disulphonic acid, is highly appreciated for its fastness to light, which is equal to that of cochineal.

The isomeric Ponceau from the R salt (commercial Ponceau 2R) is fugitive to light.

Fast Red A, $C_{10}H_6N=N-C_{10}H_6OH(\beta)$, from naphthionic acid and β -naphthol, was the first red azo dye-stuff, and is the cheapest red acid dye-stuff.

Archil Substitute is the name applied to different bluish-red dye-stuffs, corresponding to the formula :



and therefore of somewhat different composition to the Ponceaus and Bordeaux. They are readily decomposed by boiling with acids.

The practically important members of this group also include :—

Brilliant Orange R (M. L. Br.), **Scarlet R (By.)**, from xyldine and β -naphthol-6.-sulphonic acid.

Cochineal Scarlet, from xyldine and various naphthol-sulphonic acids, *e.g.*, α -naphthol-5.-sulphonic acid.

Azeosine (By.), from o. anisidine and α -naphthol-4.-sulphonic acid.

Azogrenadine S (By.), Lanafuchsine (C.), Sorbine Red (B.), from p. amidoacetanilide and α -naphthol-3. 6.-disulphonic acid.

Azogrenadine L (By.), from p. amidoacetanilide and 3. 4. naphtholsulphonic acid.

Double Ponceau (By.), from α -naphthylamine and 1. 5. naphtholsulphonic acid.

Crystal Ponceau, from α -naphthylamine and β -naphthol-6. 8.-disulphonic acid.

Brilliant Ponceau 4R (C., By.), from naphthionic acid and β -naphthol-6. 8.-disulphonic acid.

Ponceau 6R (M. L. Br.), from α -naphthylamine and β -naphthol-3. 6. 8.-sulphonic acid.

Double Brilliant Scarlet G (Act.), Scarlet for silk (M. L. Br.), Fast Red B (B.), Bordeaux BL (C.), Bordeaux G (Dahl), etc., from 2. naphthylamine-6.-sulphonic acid and β -naphthol.

Brilliant Ponceau 4R, Double Brilliant Scarlet 4R (By.), Double Scarlet extra S (Act.), from 2. naphthylamine-6.-sulphonic acid and 2. naphthol-4.-sulphonic acid.

Palatine Red (B.), from α -naphthylamine and 1. naphthol-3. 6.-disulphonic acid. This is very like Azo Red A (C.).

Fast Red BT (By.), from α -naphthylamine and 2. 6. naphtholsulphonic acid.

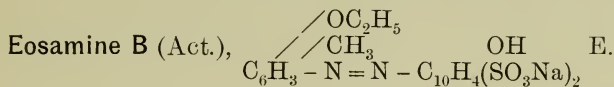
Fast Red B (B.), Bordeaux B (Act.) (M. L. Br.), Bordeaux BL (C.).

Bordeaux G (Dahl), from α -naphthylamine and β -naphthol-3. 6.-disulphonic acid.

Crimson B (By.), Mars Red (B.), Chromotrope FB, Brilliant Crimson (M. L. Br.), Azorubine A (C.), Azorubine S (Act.), etc., from naphthionic acid and 1. 4. naphthol-sulphonic acid.

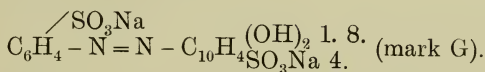
Fast Red E (By., B.), Fast Red S (M. L. Br.), from naphthionic acid and 1. 4. naphtholsulphonic acid.

Fast Red NS (By.), **Fast Red D** and **EB** (B.), **Naphthol Red S** (B.), **Naphthol O** (M. L. Br.), **Victoria Rubine** (M. L. Br.), **Bordeaux** (Act.), **Azoacid Rubine** (Dahl), etc., from naphthionic acid and 2. naphthol-3. 6.-disulphonic acid.



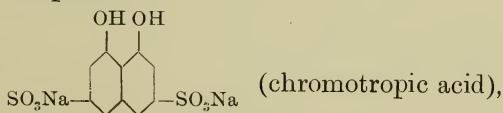
If a dioxynaphthalene sulphonic acid be employed as the second component in the preparation of such azo dye-stuffs, the resulting products are more bluish-red in colour, and are of considerable technical importance. The sulpho acids of 1. 8. dioxynaphthalene have proved especially valuable in this respect.

A dye-stuff of this kind is **Azofuchsine** (Farbenfabriken, form. Fr. Bayer & Co.),



On replacing the sulphanilic acid by toluidine sulphonic acid as the first component the B mark is obtained. Azofuchsine (the G mark in particular) enjoys an extensive application, especially for mixed colours on cashmeres and for bottoming indigo dyeings.

If the 1. 8. dioxynaphthalenemonosulphonic acid employed be replaced by a dioxynaphthalenedisulphonic acid of the following composition,



the "chromotropes" of the Farbwerke (form. Meister, Lucius and Brüning) are obtained. These are composed on the following typical plan: $\text{C}_6\text{H}_5\text{N} = \text{N} - \text{C}_{10}\text{H}_3(\text{SO}_3\text{Na})_2 \begin{array}{c} (\text{OH})_2 \text{ 1. 8.} \\ \text{2.} \end{array}$. Aniline is replaced by p. nitraniline, acetyl-p.-phenalenediamine, α -naphthalene, naphthionic acid, etc.

Both the dye-stuffs from 1. 8. dioxynaphthalemono-sulphonic acid, and those from chromotropic acid, exhibit an interesting peculiarity. Wool dyed with these in an acid bath is red, more or less tinged with blue. On treating this with potassium bichromate, it is converted into dark blue to black. These dark shades, notwithstanding their beauty and fastness, are not employed in practice (except the special mark "Chromotrope S," intended for black), their price being too high. A similar colour change on treating with potassium bichromate and sulphuric acid is exhibited by the red azo dyes from *α*-naphthol-*α*-mono-sulphonic acids, such as Chromotrope FB (M. L. Br.), Crimson (By.) (from 1. 4. naphtholsulphonic acid) and Chromotrope F4B (from 1. 5. naphtholsulphonic acid and *α*-naphthylamine), which find considerable employment on this account.

Of considerable value in practice for the production of mode colours on light woollens are the fuchsine red dyes furnished by the chromotropes in an acid bath. Their capacity for equalising and combining is excellent, and the colours they produce are clear and particularly fast to light. Peculiarly enough they are unsuitable for dyeing silk.

To this class also belong the following dye-stuffs:—

Victoria Violet 4BS (M. L. Br., By.), from paraphenylenediamine and chromotropic acid.

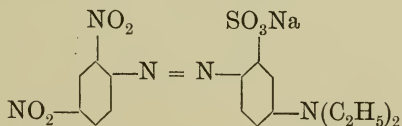
Fast Acid Fuchsine B (By.), from aniline and 1. 8. amidonaphthol-3. 6.-disulphonic acid.

Anthracene Chrome Black (C.), from 2. 3. amidonaphthol-6.-sulphonic acid and (alkylised) 1. 8. amidonaphthol-3. 6.-disulphonic acid.

Of newer dye-stuffs the following may perhaps also be included here: Fast Alkali Red (M. L. Br.), Brilliant Archil C (C.), Tolan Red (K.), Guinea Red 4R (Act.).

The employment of dioxy- and amido-oxynaphthalenesulphonic acids of the peri series has led to the production of bluish-red, blue, and even black, monoazo dye-stuffs, whereas formerly the only way to obtain such azo dye-stuffs was by piling up azo groups in the molecule. Diazotised 1. 8. amidonaphthol-3. 6.-disulphonic acid gives with secondary α -naphthylamine Lanacyl Violet (C.), with 1. 5. amidonaphthol Lanacyl Blue (C.); with alkylated 1. 8. naphthylamine sulphonic acid the Sulphonic Acid Blues (By.); asymmetrically dialkylated p. phenylenediamine gives with 1. 8. dioxy-naphthalenesulphonic acid Pure Blue dye-stuffs, *e.g.*, azo acid blue (By.); nitrodiamidophenols and their sulpho acids (from 1. 2. amidophenol) give, with peri derivatives, dye-stuffs that furnish blue colours fast to light, either by after treatment with copper salts, as is the case with Cyprus Blue (Act.), or when mixed with copper sulphate like Peri Wool Blue (C.). Diazotised picraminic acid gives with 1. 8. amidonaphtholsulphonic acids black dye-stuffs, *e.g.*, Acid Azo Black L (M. L. Br.).

The peri derivatives, however, are not the only ones capable of deepening the colour of monoazo dye-stuffs. Mention may here be made of a product introduced by the Badische Anilin- und Sodafabrik under the name of Wool Violet, but withdrawn on being found unsuitable for use (being readily decomposed by acids). This dye-stuff was produced from dinitraniline and diethylmetanilic acid, and therefore had the following constitution:—



In connection with the question of the relation between colour and constitution, it is a matter of great interest to note that this dye-stuff furnishes violet-red dyeings, whereas

hitherto none but yellow monoazo dyes had been obtained from benzol derivatives.

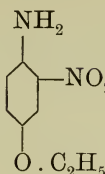
All the foregoing azo dye-stuffs are acid dyes, soluble in water by reason of their contained sulpho group, which, however, is also the cause of their low affinity for cotton fibre. Now, if non-sulphonated components be employed in their production, the resulting products are of similar dyeing properties, but being insoluble cannot be applied direct to the fibre, though they can readily be produced on the cotton itself. This method is employed to produce dyeings of considerable beauty and fastness, which now play a great part in dyeing cotton piece goods and in calico printing (Ice colours), and in this respect form dangerous competitors of the alizarine dyes.

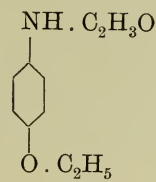
To these belong :—

Nitraniline Red, $\text{C}_6\text{H}_4 - \overset{\text{NO}_2}{\underset{|}{\text{N}}} = \text{N} - \text{C}_{10}\text{H}_6\text{OH}(\beta)$. This dye-stuff is, of course, not sold in the finished state for dyeing, but in the form of its components, nitraniline* and β -naphthol. When the nitraniline has been mixed with the quantity of sodium nitrite necessary for its subsequent diazotisation, it is termed “Nitraniline N”. Diazotised nitraniline is met with in commerce as Azophore Red† (M. L. Br.) and Nitrazol (C.). The finished nitraniline red dye-stuff, however, is put on the market by the Farbwerke (form. Meister, Lucius & Brüning) as “Discharge Lake R” and RR (in paste) for use instead of vermilion in indigo discharge printing. A similar product is Phenetidine Red (M. L. Br.), a very handsome bluish red dye-stuff prepared from nitrophenetidine and β -naphthol.

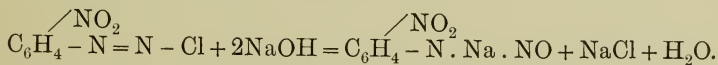
* The mark GG is meta-, whilst R is paranitraniline.

† Put on the market as Azogene Red by Kalle & Co.

The first-named component, , is prepared from

phenacetine, , by nitration and eliminating the acetyl group.

Nitrosamine Red.—This dye-stuff, which also possesses theoretical interest, and was introduced by the Badische Anilin- und Sodafabrik, owes its discovery to the already mentioned property of the diazo compounds of being transformed by the action of alkalis into the stable nitrosamine condition. The Nitrosamine Red in Paste of the above firm consists of the sodium salt of p. nitrophenylnitrosamine, $\text{C}_6\text{H}_4 - \text{N}(\text{NO}_2) \cdot \text{Na} \cdot \text{NO}$, resulting from the action of caustic soda on p. nitrodiazobenzol chloride:—



On treating this product with an acid, it acquires—by the transformation of the nitrosamine form into the diazo form—the capacity of furnishing dye-stuffs in conjunction with phenols. If β -naphthol be employed for this purpose, the resulting red is identical with nitraniline red. The unacidified nitrosamine paste can, however, be printed along with β -naphthol on the fabric, and the dye afterwards developed by acids.

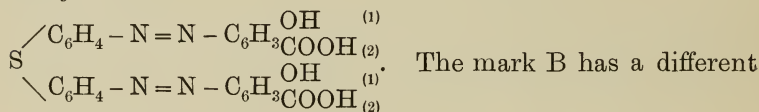
The combinations of α -naphthylamine and β -naphthol for garnet and of nitraniline with 1. 6. and 1. 7. amido-naphthol for black can be used in an analogous manner in calico printing.

YELLOW MORDANT AZO DYE-STUFFS.

To this class belong a number of dye-stuffs prepared by the aid of salicylic acid, and mainly intended to serve as fustic substitutes in wool dyeing.

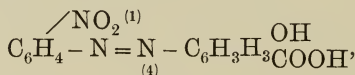
The chief member of the group is:—

Anthracene Yellow C (C.), Fast Chrome Yellow C (C.), Fast Mordant Yellow (B.), from diazotised thioaniline and salicylic acid.



composition (see below), whilst the mark R is a mixture.

Alizarine Yellow GGW (M. L. Br.),



from metanitrilaniline and salicylic acid. The mark R is prepared from paranitrilaniline.

Diamond Yellow (By.), $\text{C}_6\text{H}_4 - \text{N} = \text{N} - \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{COOH} \begin{smallmatrix} (1) \end{smallmatrix} \\ \text{COOH} \end{smallmatrix} \begin{smallmatrix} (4) \end{smallmatrix}$ from para-amidobenzoic acid and salicylic acid.

Chrome Yellow D (By.), Mordant Yellow (B.), Mordant Yellow O (M. L. Br.), Milling Yellow (Dahl), Anthracene Yellow BN, $\text{C}_{10}\text{H}_6 - \text{N} = \text{N} - \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{SO}_3\text{Na} \\ \text{COOH} \end{smallmatrix} \begin{smallmatrix} \text{OH} \end{smallmatrix}$ from 2. naphthylamine-6.-sulphonic acid and salicylic acid.

Flavazol (Act.), $\text{C}_6\text{H}_4 - \text{N} = \text{N} - \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{CH}_3 \\ \text{COOH} \end{smallmatrix} \begin{smallmatrix} \text{OH} \end{smallmatrix}$ from p. toluidine and salicylic acid.

Fast Chrome Yellow GG (Act.) from o. anisidine and salicylic acid.

Quite a special position among the azo dye-stuffs is occupied by a product that is no longer on the market, but

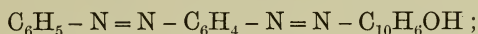
was named **Patent Fustine** (Wool Yellow (B.)) and was prepared by the action of diazo compounds on fustic extract in presence of soda.

TETRAZO DYE-STUFFS.

The dye-stuffs of this group are of acid character, and contain two acid groups; they are red to black in colour, and, for the sake of convenience, will be dealt with in two divisions.

1. *Red Dye-stuffs.*

These, for the most part, give scarlet red dyeings, which are generally faster to light than those obtained with the monoazo dye-stuffs already described. Almost without exception they contain the atomic complex:—



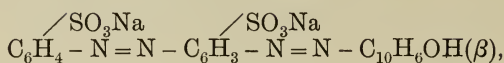
wherein the SO_3H group or groups may be present in various positions, either in one or other of the nuclei, or in several simultaneously. Consequently in their preparation, use is made of amidoazobenzol and its homologues, and sulpho acids, as the first components, with β -naphthol and its sulpho acids (chiefly: 2. naphthol-6., -6. 8., -3. 6. 8.-sulphonic acids).

The position of the sulpho group influences the colour furnished by these dye-stuffs with concentrated sulphuric acid: such of them as contain the sulpho groups in the benzol nuclei are coloured green by sulphuric acid; those containing the one or more sulpho groups in the naphthalene nucleus are stained violet; whilst those wherein the sulpho groups occur both in the benzol and the naphthalene nuclei are coloured blue with the acid in question.

The following may serve as examples:—

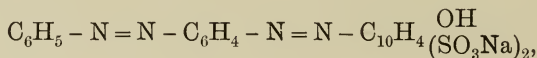
Biebrich Scarlet, **Old Scarlet** (By.), **Fast Ponceau B**

(B.), Ponceau B extra (M. L. Br.), Scarlet EC (C.), etc.,



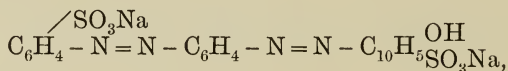
are coloured green by concentrated sulphuric acid.

Brilliant Croceine M (C.), **Brilliant Croceine 3B** (By.), **Brilliant Croceine**, bluish tinge (M. L. Br.), **Cotton Scarlet B.** (K.), etc.,



from amidoazobenzol and 2. naphthol-6. 8.-disulphonic acid, are coloured violet by concentrated H_2SO_4 .

Croceine Scarlet 3B (By.):—



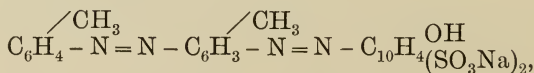
from amidoazobenzolsulphonic acid and 2. naphthol-8.-sulphonic acid.

The mark 7B is prepared from amidoazotoluol as first component.

The B marks of Bayer's Croceine Scarlet are identical with the RB Ponceaus of the Berliner Act. Ges. für Anilinfabrication; whilst the R marks of Bayer's Ponceaus are identical with the BX marks of the other firm's Croceine Scarlet.

Others belonging to this group are, Bayer's Bordeaux G, from amidoazotoluolsulphonic acid and 2. naphthol-6.-sulphonic acid, and the mark BX from amidoazoxyloldisulphonic acid and β -naphthol.

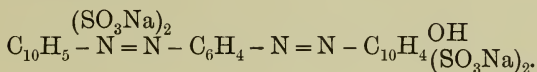
A brown dye-stuff that is also fixed with chrome mordants is **Cloth Red B** (Oe., By.),



from amidoazotoluol and 2. naphthol-3. 6.-disulphonic acid. It is used to replace santal in wool dyeing.

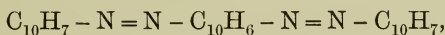
An instance of a red tetrazo dye-stuff of this group with two naphthalene nuclei is afforded by

Brilliant Croceine 9B (C.), which is prepared from 2. naphthylamine-6. 8.-disulphonic acid, and consequently exhibits the formula :—



2. Black Dye-stuffs.

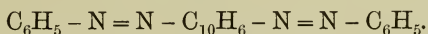
The dye-stuffs of this group contain the atomic complex :—



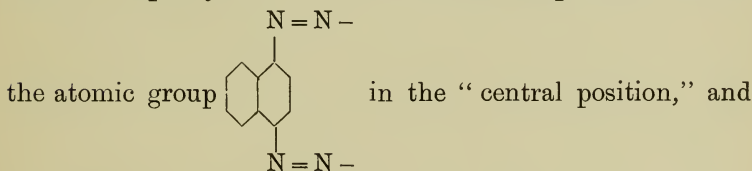
or



or



They are asymmetrical diazo compounds, which, by the use of *a*-naphthylamine as the second component, contain



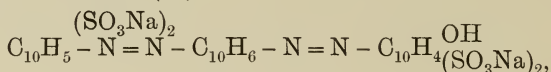
thus differ considerably from the red tetrazo dye-stuffs previously considered. They are also in general much faster than these latter. Sulpho acids of naphthylamine and aniline are mostly used as the first components, various naphthol sulphonic acids being generally taken as third or "terminal" components. The "intermediate" components most in use are *a*-naphthylamine and its sulpho acids—1. naphthylamine-6. and 7.-sulphonic acid.

The application of special components (*e.g.*, 2. amido-5.-naphthol-7.- sulphonic acid) as terminals leads to the formation of salt dyes.

The method of preparation consists in combining the first component as a diazo compound with the second component to form an amidoazo compound. This is then diazotised again, and coupled with the third (terminal) components.

To this class belong:—

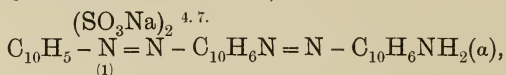
Naphthol Black (C.),



from 2. naphthylamine-6. 8.-disulphonic acid, α -naphthylamine, and 2. naphthol-3. 6.-disulphonic acid. It was the first technically important dye-stuff of the group. Its dyeings are fast to light, but not particularly so to milling and washing.

Brilliant Black B (B.) is identical with Naphthol Black, and the other marks of this dye-stuff are mixtures of various acid dyes.

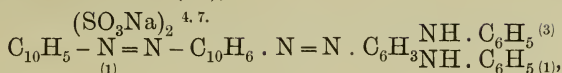
Naphthylamine Black D (C.),



can be applied in the same way as naphthol black. The dyeings are faster to milling, though less so to acid, and less handsome than those of this latter.

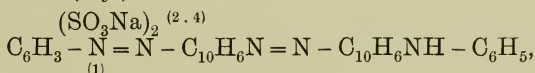
The highly appreciated and important mark 4B is a mixture of the above Naphthylamine Black with the Naphthol Blue-Black to be described later on. Its principal advantage is the handsome logwood shade of its dyeings.

Naphthyl Blue-Black N (C., By.) is of similar composition to Naphthylamine Black D, except that it contains, instead of α -naphthylamine, the ethyl ether of this latter as terminal component. When dyed along with acetic acid, it furnishes a very handsome bluish-black, which, when afterwards treated with copper salts, is very fast to light, though very susceptible to the action of steam. It is very largely used in this way.

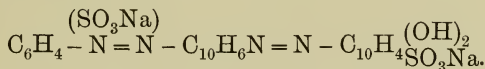
Anthracite Black (C.),

from 1. naphthylamine-4. 7.-disulphonic acid, α -naphthylamine and diphenyl-m.-phenylenediamine.

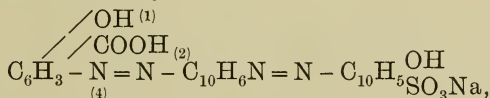
This can be used for dyeing wool with or without mordants. It is, however, not employed for black dyeing this fibre, but is used in association with Fast Diamine Red F and Anthracene Yellow C (same makers) for the preparation of wool dyes fast to milling.

Jet Black (By.),

from aniline-2. 4.-disulphonic acid, α -naphthylamine and phenyl- α -naphthylamine. This is suitable for dyeing silk dark blue or black on the small scale, and also gives a handsome blue-black on wool. The dye-stuff is sensitive to metals.

Victoria Black (By.),

The different marks of this dye-stuff contain, as characteristic component, 8. dioxynaphthalene-4.-sulphonic acid. Other amidosulphonic acids are also used in place of sulphanilic acid. These dyes are intended for black on wool.

Diamond Black (By.),

from amidosalicylic acid, α -naphthylamine and 1. naphthol-4. or 5.-sulphonic acid.

This dye-stuff, which is very important by reason of its great fastness to light, is very largely used as a chrome lake in wool dyeing. The Diamond Green of the same maker is

prepared in the same manner, with 1. 8. dioxynaphthalene-4-sulphonic acid as terminal component.

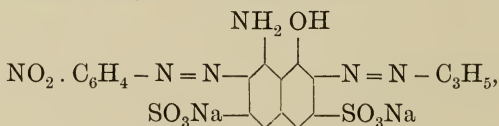
Dye-stuffs similar to Diamond Black are furnished by amidoparaoxybenzoic acid, amidobenzoic acid and amidophthalic acid.

When the Diamond Black dyes are afterwards treated with potassium bichromate and sulphuric acid, the formation of the chrome lake is accompanied by oxidation, which increases their tinctorial power and fastness.

Sulphone Black (By.), a new dye-stuff of this group, is prepared with a peri derivative in the terminal position.

With regard to the technical novelties in this group mention may first be made of the use of p. amidodiphenylaminesulphonic acid as first component. This furnishes dye-stuffs specially fast to washing and suitable for the dyeing of knitting yarns. **Nerol Black (Act.)** belongs to this class.

Furthermore, the behaviour (already described) of certain amidonaphtholsulphonic acids in the coupling process has led to a new method of preparing the dye-stuffs of this group. Thus, for example, 1. 8. amidonaphthol-3. 6.-disulphonic acid is first combined with p. nitrodiazobenzol in acid solution, and then to a tetrazo compound with one of the numerous azo components—the latter in the state of a diazo compound—in alkaline solution. By taking diazobenzol in the final stage, Cassella's **Naphthol Blue-Black**,

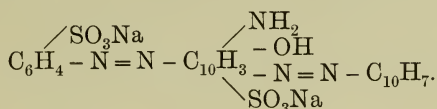


is obtained. Naphthylamine Black 4B, the most largely employed substitute for logwood in wool dyeing, is a mixture of the above dye-stuff with Naphthylamine Black D.

A Palatine Black* (B.), which belongs to the more fugitive members (towards light) of this group, is prepared from

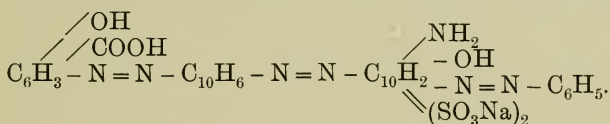
* The commercial dye-stuff sold under this name is not uniform.

1. 8. amidonaphthol-4-sulphonic acid, by first treating the same with diazosulphanilic acid and then with diazotised α -naphthylamine in a faintly acid solution:—



Wool Black 6B (Act.) is of analogous composition.

In this connection, peculiar behaviour is exhibited by the so-called K-acid (1. 8. amidonaphthol-4. 6-disulphonic acid), inasmuch as this will not combine with diazosalicylic acid except with difficulty; in fact, this can only be successfully accomplished in practice by indirect means—as is the case with Kalle's Patent Chrome Green. Here the diazosalicylic acid is first coupled with α -naphthylamine, then diazotised, and the resulting diazo compound treated with the azo compound from K-acid and aniline. The formula is therefore:—



Other dye-stuffs belonging to the tetrazo class are: Naphthylamine Black S, Anthracene Acid Black (L. Cassella & Co.); Biebrich Patent Black—several marks of which are mixtures—(Kalle & Co.); Phenol Black SS (Fr. Bayer & Co.); several Wool Blacks of the Berliner Act. Ges. für Anilinfabrication; the Acid Black of the Ges. f. Chem. Ind. Basel, etc. Dahl's Wool Black is identical with Naphthol Black; Bayer's Naphthalene Acid Black (4B and S) and Phenylamine Black (4B and T) are mixed products, as are also Palatine Black (B. A. S. F) and most of the logwood substitutes.

All these dye-stuffs—starting from Naphthol Black—are intended to replace logwood in dyeing wool.* This has in

* An acid bath is used, and in some cases an after-treatment with chrome is given.

part already proved successful. Logwood has been almost entirely superseded in wool printing by Naphthylamine Black and others; and several of the above-named dye-stuffs are used for black, a few of them—*e.g.*, Naphthol Black and the Cheap Phenol Black—also for navy blue on a large scale. A successful competitor is Hoechst Azo Acid Black (a mixture of various dye-stuffs), which is largely used on account of its handsome shade and good distributing power.

SUBSTANTIVE COTTON DYE-STUFFS.

Up to the year 1884 it was always necessary to put cotton through a preparatory treatment before dyeing. There are only three natural dye-stuffs (curcuma, safflower and Orleans) that can be used for dyeing cotton without the aid of a fixing material, since the dyeings produced by many of the artificial dye-stuffs (Methylene Blue, Safranine, Bismarck Brown) on unprepared cotton are insufficiently fast and intense to be of any practical importance.

In the year in question Böttiger discovered Congo Red, the first dye-stuff of a whole series, all of which possess the valuable property of producing an intense colour on cotton without the use of fixing agents. Similar dye-stuffs, moreover, had already been described in 1883, in the German patent, No. 27,954, taken out by the Farbenfabriken, form. Fr. Bayer & Co. (Duisberg), at the instigation of P. Griess.

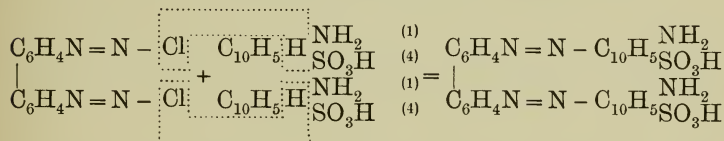
These dye-stuffs having been derived from benzidine received the name benzidine dye-stuffs. It was soon found, however, that a whole series of other bases, some of them allied in composition to benzidine, others more remote, could also be converted into dye-stuffs of equal tinctorial capacity, and for this reason the name substantive cotton dye-stuffs was selected. This term is, however, not altogether applicable, some of them being

more suitable for wool than for cotton; and, in view of their mode of application (with an addition of neutral or alkaline salts), they are more suitably termed salt dye-stuffs.

It is in this domain that the dye-stuff industry of the present day reaps its most abundant harvest.

Congo Red is produced when benzidine, $\begin{array}{c} \text{C}_6\text{H}_4 - \text{NH}_2 \\ | \\ \text{C}_6\text{H}_4 - \text{NH}_2 \end{array}$, is

diazotised, and two molecules of naphthionic acid are allowed to react on the resulting tetrazodiphenyl chloride:

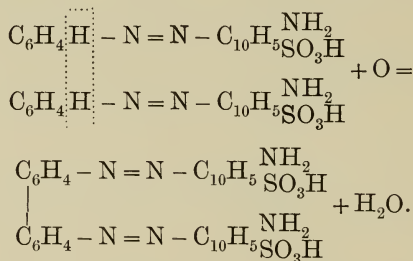


The sodium salt of this body constitutes Congo Red.

In the preparation of this, as in the case of all similar dye-stuffs, the second component—the amine or phenol—must react during some time on the tetrazo compound, since, though the reaction on the first molecule of the second component is quickly accomplished, time is required for combination with the second molecule. With Congo Red, for example, the operation takes one to two days, and with the Benzopurpurine, to be described later, five to six days are required. If a large excess of naphthionic acid be employed, the second process is accelerated. The resulting first intermediate product, which therefore still contains one free diazo group, is generally insoluble. It can be isolated and then employed for the purpose of reacting on a further molecule of the same or of another component. In this second reaction it is generally necessary to employ a temperature of 50° C., the mixture being stirred until the evolution of nitrogen has ceased. In most cases it is

not altogether a matter of indifference whether the operation of coupling is performed in an acid or alkaline solution.

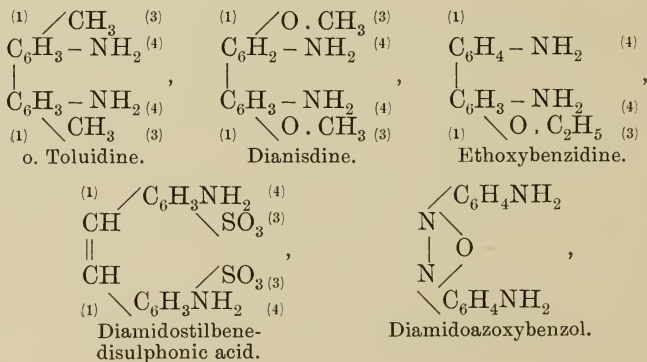
According to a very surprising discovery made by the Badische Anilin- und Sodafabrik, these dye-stuffs are also formed by the oxidation of simple azo dye-stuffs in concentrated sulphuric solution, with manganese peroxide in the cold. The dye-stuff resulting from diazobenzol and naphthionic acid hereby gives Congo Red:



Similarly the dye-stuff from o. toluidineazo-naphthionic acid furnishes Benzopurpurine 4B.

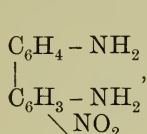
Compared with the direct method the process is too costly. Frequently also a chaining of other nuclei occurs, and furnishes valueless dye-stuffs.

Instead of benzidine a large number of other more or less similar bases can be employed in the production of those dye-stuffs, chief among them being:—

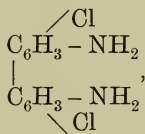


m. and p. phenylene- (or toluylene-) diamine and a few naphthylenediamines.

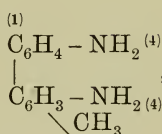
In addition to these the following bases have also found employment :—



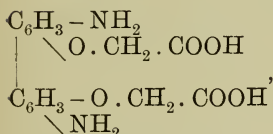
Nitrobenzidine.



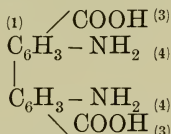
Dichlorbenzidine.



Diamidophenyltoluyl.

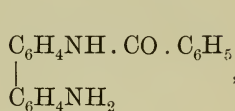


Diamidodiphenoxylactic acid.

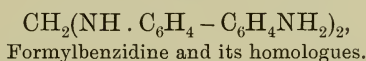


Benzidinededicarbonic acid

(Naphthol Blue, B.A.S.F.).

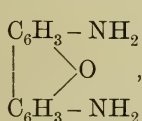


Benzylbenzidine.

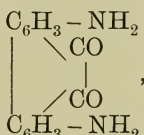


as also mixed condensation products, *e.g.*, of formaldehyde, dianisidine and aniline.

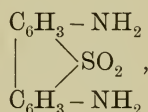
Use is also made of bases, which may be regarded as benzidine in which two benzol nuclei are chained, by a divalent group or element in the ortho position to the point of linking :—



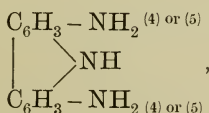
Diamidodiphenylene-oxide.



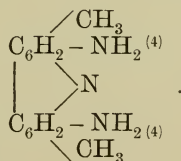
Di-p.-diamidophen-anthrenequinone.



Diamidobenzo-sulphone.

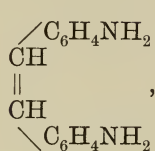


In the position (5) of the amido groups, base of Carbazol Yellow.

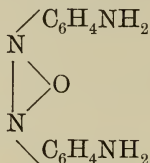


p. Diamidodimethyl-carbazol.

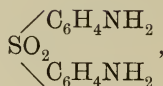
In other bases again the benzol nuclei are not (as in benzidine) in direct mutual connection.



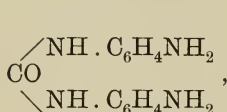
Diamidostilbene.



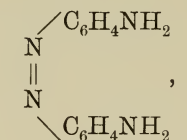
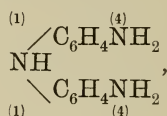
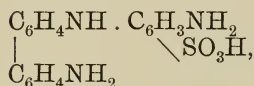
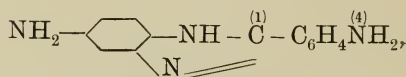
Diamidoazoxybenzol.



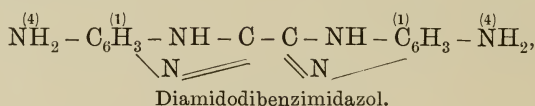
Diamidosulphobenzide.



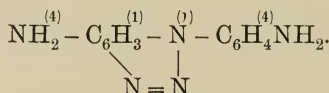
Diamidodiphenylurea.

Symmetrical
Diamidoazobenzol.p. Diamidodi-
phenylamine.Amidophenylbenzidine-
sulphonic acid.

Diamidophenylbenzimidazol.



Diamidodibenzimidazol.



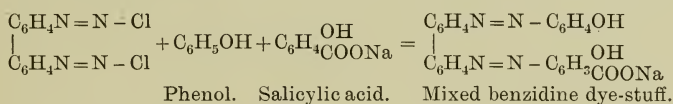
Diamidophenylazimidobenzol.

The bases of the naphthalene series corresponding to benzidine, *i.e.*, the “dinaphthyles,” are unsuitable for the production of usable substantive cotton dye-stuffs.

Still more numerous than the diazotisable bases suitable for the production of substantive cotton dye-stuffs are the amines, phenols and their sulpho acids that can be used as second component. Chief among these are the sulpho acids of the naphthols, naphthylamines, dioxy-, amidoxy- and diamidonaphthalenes (among the latter principally the peri

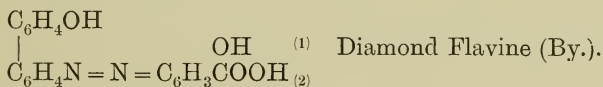
derivatives). Since we are now acquainted with 88 naphthol- and naphthylamine sulpho acids and 85 dioxy-, amidooxy- and diamidonaphthalene sulpho acids, it is very evident that the number of possible combinations must be very considerable. These are still further augmented by the fact that simple benzol derivatives, such as phenol, resorcline, salicylic acid, salol, etc., also find employment for the same purpose.

Finally, the already mentioned peculiarity of the formation of these bodies in two phases can be utilised for so-called mixed combination, by allowing two different components to react on each molecule of the diazotised base, instead of acting on both by one and the same phenol or amine, *e.g.* :—



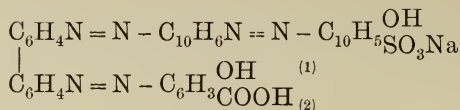
Here, however, in many instances (see Anthracene Red), it is by no means immaterial which of the two components is allowed to react first.

If only one molecule of an amine or phenol be allowed to react on the tetrazo compound, and the residual free diazo group be afterwards replaced by hydroxyl, we obtain simple azo compounds, which, however, still possess to a small extent the property of the benzidine dye-stuffs of dyeing cotton without the aid of a fixing agent, *e.g.* :—



Finally, use is made, for the production of still more complex azo dye-stuffs, of the property of possessing a diazotisable group exhibited by several of the bodies employed in the preparation of these dyes.

The following formula may serve as an example of their composition :—



Along with these dye-stuffs may be classed two other groups of salt dye-stuffs, the thiazol dyes and azoxystilbene dyes, which, however, must be dealt with separately, on account of their very different composition.

The number of *possible* salt dye-stuffs is therefore immeasurably great; and at the present time over 600 are known in commerce.

The most numerous are the blues and blacks, followed in order by the browns, reds, yellows, violets, oranges and greens.

They are all employed in the form of alkali salts, mostly of sodium, and also fix themselves as such on the cotton fibre. Only a few of them are used for dyeing wool and silk.

The pigmentary character of the dye salts is mainly influenced by the diazotised base, sometimes, however, also by the other components. Since whilst, for example, the Biebrich Scarlet is not a dye salt, a strong affinity for cellulose

is exhibited by the dye-stuffs $\text{C}_6\text{H}_4-\overset{\text{SO}_3\text{Na}}{\text{N}}=\text{N}-\text{C}_6\text{H}_4\text{N}=\text{N}-\text{X}$, in which the position X is occupied by nitrometaphenylenediamine or 2. ethylamido-5.-naphthol-7.-sulphonic acid. In any event the para position of the nitrogen plays an important part, and consequently such dye-stuffs are frequently built up with the aid of p. nitraniline or p. amidoacetanilide. These are introduced, as diazo compounds, into a suitable atomic complex, the NO_2 being then reduced to NH_2 (or the acetyl group eliminated), diazotised and coupled with azo components.

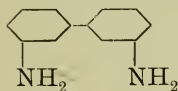
It is not quite clear from their composition why they act as substantive dyes on cotton, a fibre usually

exhibiting such a small affinity for dyes. This property cannot reside in the diphenyl group, since even the dyes

derived from diamidostilbene, $\begin{array}{c} \text{CH} - \text{C}_6\text{H}_4\text{NH}_2 \\ || \\ \text{CH} - \text{C}_6\text{H}_4\text{NH}_2 \end{array}$, possess the same

power.

Moreover, the para position of the two amido groups cannot alone be the cause, since the metadiamine,

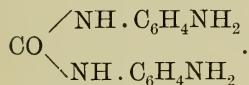


prepared by Witt and Brunner, furnishes

dye-stuffs that also exhibit the same property, though in diminished proportion.

It is remarkable that the dye-stuffs from dipara-amido-benzophenone, $\text{CO} \begin{array}{l} \text{C}_6\text{H}_4\text{NH}_2 \\ \text{C}_6\text{H}_4\text{NH}_2 \end{array}$, have no affinity for cotton

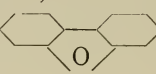
fibre, such as is possessed by those from diamidodiphenylurea,

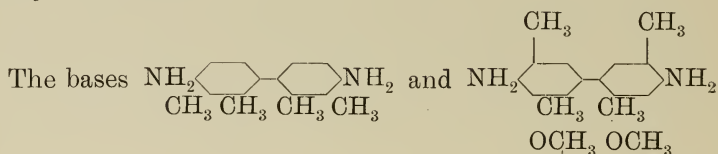


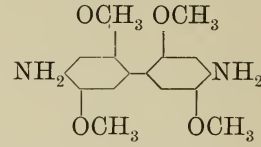
Finally, substantive dye-stuffs are known which contain only a single azo group. Consequently the affinity towards cotton cannot be due to the presence of two azo groups.

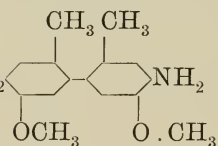
With regard to the influence exerted on the production of substantive dyes by the entry of different groups into different positions in the molecule of benzidine,* little is as yet known: if alcohol radicles or ether groups appear on the ortho position to the connecting link, their influence is inimical to the faculty in question; whereas it is favourable when they are in the meta position. Thus, for example, o. toluidine, $\text{NH}_2 - \text{C}_6\text{H}_3(\text{CH}_3) - \text{C}_6\text{H}_3(\text{CH}_3) - \text{NH}_2$, furnishes better cotton dyes than benzidine itself.

* *Berl. Ber.*, **21**, p. 3138; **23**, p. 3252; *Chem. Zeit.*, 1888, No. 25.

If sulpho groups or halogens appear in the ortho position to the connecting link, benzidine is deprived of its faculty of yielding substantive cotton dye-stuffs; however, in the case of diamidodiphenylene oxide, NH_2  NH_2 , this faculty is retained.



furnish dye-stuffs that draw badly; NH_2  NH_2 gives dyes that have a certain, though small, affinity for

cotton; NH_2  NH_2 does not yield cotton dyes.

It has, however, been found possible to establish certain simple relations between the colour on the one hand, the fastness on the other, and the composition of these dye-stuffs. The diphenyl bases furnishing substantive cotton dye-stuffs give red dye-stuffs with naphthylaminesulphonic acids, and violet to blue with naphtholsulphonic acids. The other class of bases, which furnish wool dye-stuffs but not substantive cotton dyes, give yellow to orange with naphthylamine-sulphonic acids, and red with naphtholsulphonic acids.

The fastness of these dye-stuffs exhibits the following dependence on their constitution: The yellow dye-stuffs obtained from phenol, salicylic acid, etc., are faster to light than those from naphthol- and naphthylaminesulphonic acids; the dye-stuffs from β -naphthylaminesulphonic acids are faster to acids but less powerfully tinctorial than those from α -naphthylaminesulphonic acids. The fastness to acids is still

greater when the β -naphthylamine acids are combined with o. dichlorobenzidine instead of benzidine.

Speaking generally, it may be said that the yellow and orange salt dye-stuffs are much faster to light than the reds, violets and blues, the latter mostly exhibiting this property in an inferior degree. They can, however, be rendered very fast to light by boiling the dyeings with salts of copper, zinc or nickel. Unfortunately this treatment usually alters the shade, and the beneficial influence of copper—which is almost exclusively used for this purpose—is nullified by washing.

With regard to the general properties of the salt dye-stuffs, it may also be mentioned that they act on basic dye-stuffs like a fixing agent, and that, up to the present, no poisonous properties have been detected in any of them.

SIMPLE BENZIDINE DYE-STUFFS.

Diazotised benzidine, in conjunction with simple benzol derivatives, like phenol, salicylic acid, etc., furnishes yellow dye-stuffs; with naphthylaminesulphonic acids, red; with naphthylaminesulphonic acids substituted in the NH_2 group, bluish-red to violet; with naphtholsulphonic acids, violet; and with certain amidonaphthol- and 1.8 dioxynaphthalenesulphonic acids, blue to black dye-stuffs.

Diazotised toluidine behaves in an analogous manner, except that the resulting dye-stuffs have a more bluish tinge than those from benzidine. Thus, for instance, the benzo-purpurines produced from the former by combination with naphthylaminesulphonic acids are more bluish than the Congo Red obtained from benzidine and the same components. The greatest tendency towards blue is exhibited by the dye-stuffs from dianisidine.

Consequently one is able, by mixed combinations, to

produce a whole series of dye-stuffs between red and blue; *e.g.*, toluidine and naphthylaminesulphonic acids give the (red) Benzopurpurines; toluidine and naphtholsulphonic acids, Azo Blue; hence, if 1 molecule of naphthylaminesulphonic acid and 1 molecule of naphtholsulphonic acid be allowed to react on (diazotised) toluidine, a violet dye-stuff (Congo Corinth B) is obtained.

A little acquaintance with these dye-stuffs will, therefore, frequently enable one to draw conclusions as to the colour of the dye-stuff corresponding to this formula; *e.g.*, diazotised benzidine and 2 molecules of salicylic acid give a yellow dye-stuff (Chrysamine); diazotised toluidine and naphtholsulphonic acid, a reddish-blue dye-stuff (Azo Blue); hence a mixed combination of toluidine with 1 molecule of salicylic acid and 1 molecule of naphtholsulphonic acid will give a dye-stuff, which, in view of the circumstance that Chrysamine is a stronger colour than Azo Blue, will produce a reddish-blue shade modified by yellow, and, therefore, brown (Cloth Brown).

The components most frequently used are: phenol, salicylic acid, creosotic acid, *m.* phenylene- or toluylenediamine and their sulpho acids, nitro-*m.*-phenylenediamine, 1-4 and 1-5 naphtholsulphonic acid; 1-4, 1-5, 1-6, 1-7, 2-6, 2-7, and 2-3-6 naphthylaminesulphonic acids; 2 naphthol 3-6 and 6-8 disulphonic acids; 1-8 dioxynaphthalene 4- and 3-6 sulphonic acids; 1-8 amidonaphthol -4, 2-4, 3-6, and 4-6 sulphonic acids; and 2. 8. amidonaphthol-6- and 3-6 sulphonic acids.

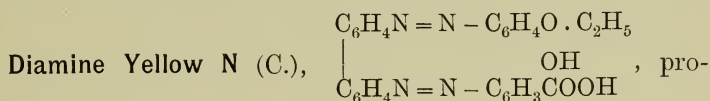
Other components, more rarely used, are: divers oxamic

acids, *e.g.*, toluyleneoxamic acid, $\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{CH}_3 \\ - \text{NH}_2 \\ \diagdown \text{NH} \cdot \text{COCOOH} \end{array}$; then

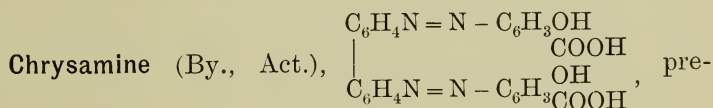
glycines, *e.g.*, *m.* amidophenylglycine, $\text{C}_6\text{H}_4 \begin{array}{l} \text{NH}_2 \\ - \text{NH} \cdot \text{CH}_2\text{COOH} \end{array}$;

phenylated, alkylated amidonaphtholsulphonic acids, mono-alkylated 1. 8. dioxynaphthalenesulphonic acids, 1. 8. chloronaphtholsulphonic acids, oxynaphthoic acids, aceto-acetic ester and similar β -diketones, and, finally, also finished dye-stuffs, principally Chrysoidine, Bismarck Brown, and resorcline azo dye-stuffs.

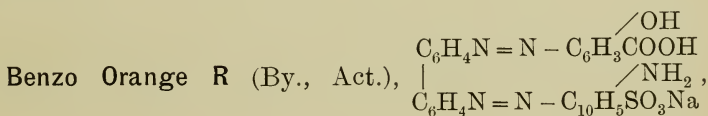
In the following list of the dye-stuffs belonging to this category the dependence of the colour on the nature of the individual components and the substituent groups will chiefly be borne in mind.



duced from benzidine, phenol- and salicylic acid, followed by ethylisation.*

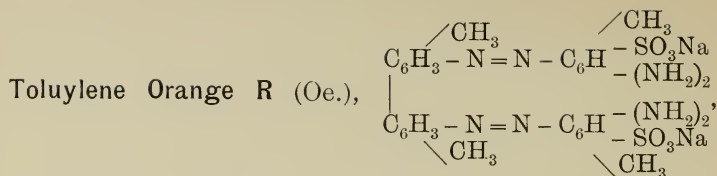


pared from benzidine and 2 molecules of salicylic acid. This is an important dye-stuff, and is principally used for the production of cream colours in calico printing. It should not be employed in copper vessels, since this metal dulls the colour.



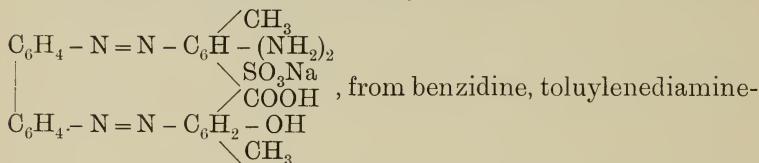
prepared from benzidine, salicylic acid and naphthionic acid.

* This dye-stuff cannot be produced direct from diazotised benzidine, salicylic acid and phenol ether; the latter does not react on diazo compounds, its behaviour in this respect being that of a hydrocarbon.

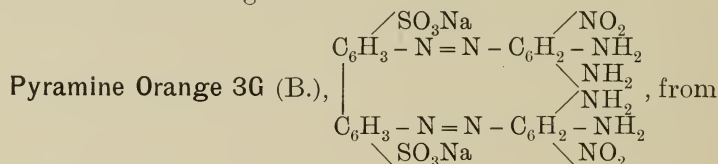


from toluidine and 2 molecules of m. toluylenediamine-sulphonic acid.

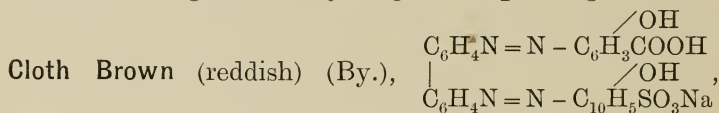
Toluylene Orange G (Oe., By., Act.),



sulphonic acid and creosotic acid, is one of the most important dye-stuffs for half-silk goods.

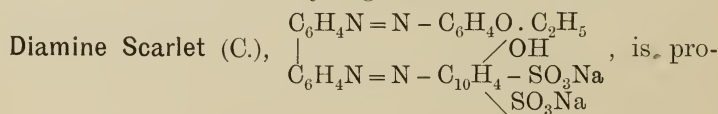


benzidinesulphonic acid and 2 molecules of nitrometaphenylenediamine. It gives a very bright cheap orange.

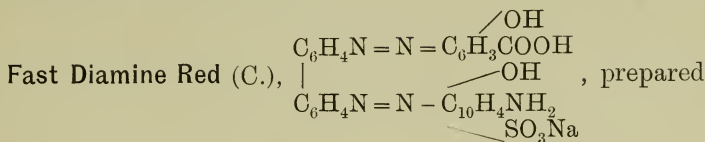


prepared from benzidine, salicylic acid and 1. 4. naphtholsulphonic acid.

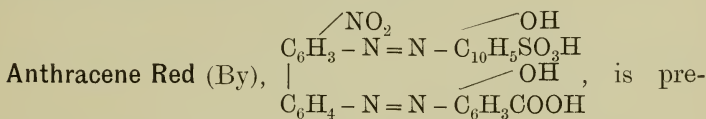
This, like the similarly constituted yellowish Cloth Brown (from 2. 7. dioxynaphthalene instead of naphtholsulphonic acid), is used for dyeing chromed wool in a weak acid bath. It therefore forms the first example of a substantive cotton dye-stuff less suitable for dyeing cotton than for wool.



duced from benzidine, phenol and 2. naphthol-6. 8.-disulphonic acid, followed by ethylisation.



from benzidine, salicylic acid and 2. 8. amidonaphthol-6.-sulphonic acid. It is a bluish-red, suitable for dyeing both cotton and wool. For the latter it can be applied in an acid bath, and fixed by after-treatment with chromium fluoride, the dyeings being then distinguished for their fastness. On cotton it is comparatively fast to light.



pared from nitrobenzidine, salicylic acid and 1. 4. naphthol-sulphonic acid. In this case it is not immaterial which of the two components is first allowed to react on the diazotised base, since salicylic acid in the second place is difficult to couple. Consequently, if the naphtholsulphonic acid be taken first and salicylic acid afterwards, an inferior dye-stuff is obtained; but by reversing the order there results the valuable Anthracene Red which is particularly suitable for wool dyeing. The dye-stuff is used in an acid bath, and can be afterwards fixed with chromium fluoride.

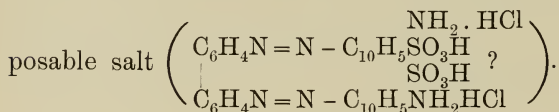
A homologous Anthracene Red is prepared by the aid of nitrotoluidine. Kalle & Co. prepare a Salicine Red from mononitrobenzidine, salicylic acid and β -naphthol. The Salicine Yellow made by the same firm is nitrobenzidine-diazosalicylic acid.

Fast Diamine Red and Anthracene Red are much faster to acids than the red benzidine dye-stuffs now to be described.

Congo Red (A., By.), $\left| \begin{array}{l} \text{C}_6\text{H}_4\text{N}=\text{N}-\text{C}_{10}\text{H}_5\text{SO}_3\text{Na}^{(1)} \\ \text{C}_6\text{H}_4\text{N}=\text{N}-\text{C}_{10}\text{H}_5\text{SO}_3\text{Na}^{(1)} \end{array} \right|$, is produced

from benzidine and 2 molecules of naphthionic acid. It is the first dye-stuff of this series; was discovered by Böttiger in 1884, and first put on the market by the Berlin Actiengesellschaft für Anilinfabrication. A characteristic property of this dye-stuff is that its dyeings (as also the dye-stuff itself) are turned blue by the slightest trace of an acid.

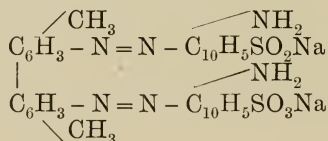
The original colour is partly restored by washing with water, and the blue coloration may therefore be attributed with some probability to the formation of a readily decom-



This sensitivity towards acids renders Congo Red useful on the one hand as an indicator, but on the other diminishes its practical value as a dye-stuff. Nevertheless large quantities of the dye-stuff are made, chiefly for export to Eastern Asia.

Of greater practical importance, since less sensitive to acids, are a whole series of benzidine dye-stuffs, chief among them being the

Benzopurpurines (By., Act.). These were discovered shortly after Congo Red, by Duisberg, and correspond in composition with the following formula:—

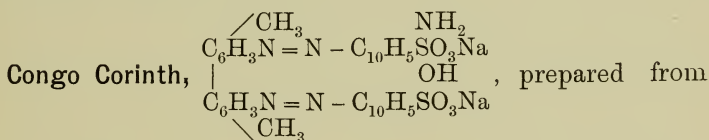


The important mark 4B is prepared from toluidine and 2 molecules of naphthionic acid, and is also met with in commerce under the name of Cotton Red 4B (B.). A number of very similar dye-stuffs contain, instead of naphthionic acid,

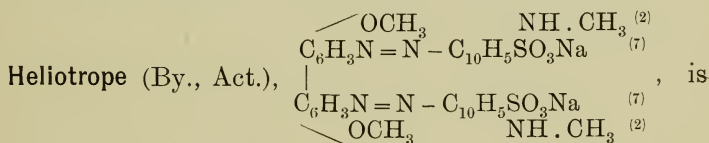
other naphthylaminesulphonic acids or also benzol derivatives; for example, Congo Red 4B, which is made from toluidine, naphthionic acid and resorcine.

Of this kind are various Congo marks, such as Brilliant Congo (By., Act.), also Brilliant Purpurine (Act.), Delta Purpurine, 5B (By., Act.), Diamine Red 3R (C.), etc. They find extensive employment, especially in the imitation of Turkey red in cotton dyeing.

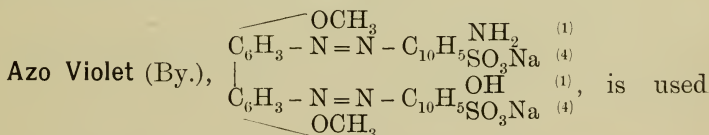
As an example of the dye-stuffs derived from dichlorobenzidine may be cited Toluylene Red (Oe.), Acetopurpurine (Act.), which is produced by coupling the base in question with 2 molecules of 2. naphthylamine-3. 6.-disulphonic acid, and is very fast to acids.



toluidine, 1. naphthylamine- and 1. naphthol-4.-sulphonic acid. This is a brownish-red, which finds employment in the production of Bordeaux shades on cotton. Isomeric with it is the Congo Rubine of Fr. Bayer & Co.

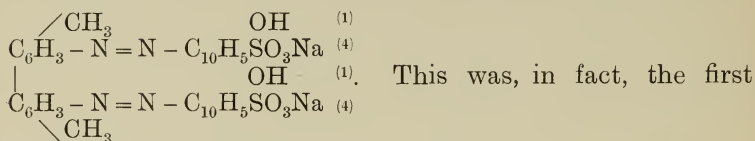


of a still more bluish tinge than the foregoing, and is well adapted for the production of pale heliotrope shades on cotton (particularly the mark BB).



in the cotton dyeing industry for deepening shades.

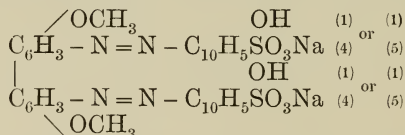
If 2 molecules of naphtholsulphonic acid be allowed to react on diazotised toluidine, the product forms the first blue benzidine dye-stuff (discovered by Duisberg), *viz.*, Azo Blue,



blue azo dye known.

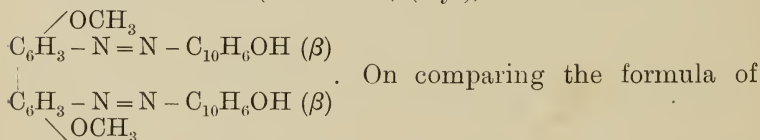
It is only applicable to cotton, and, by reason of its ugly reddish shade, is merely of low value.

The **Benzazurine** (By.), discovered by Duisberg,



was the first valuable blue benzidine blue dye-stuff known. It is a purer blue than the one last named, but still too reddish in tinge to be used in the preparation of green. It plays a great part in cotton dyeing. The colours are rather fugitive to light, and are turned red by alkali, for which reason special importance attaches to the after-treatment with copper already mentioned in connection with this group of dye-stuffs. When thus treated the fastness of the benzazurine dyeings to light is extremely good. Another peculiarity exhibited by these dye-stuffs is that their dyeings assume a reddish tinge when hot-ironed, reverting, however, to the original beautiful blue shade on cooling.

Dianisidine Blue (M. L. Br.) (By.),



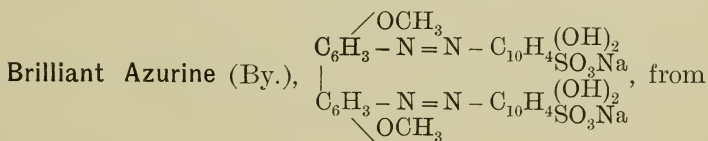
this dye-stuff with that of Benzazurine, it is seen that their composition is identical, up to the sulpho groups and the

position of the OH groups ; however, as already stated, the sulpho groups, though in many cases having little effect on the character of a dye-stuff, influence its solubility in water.

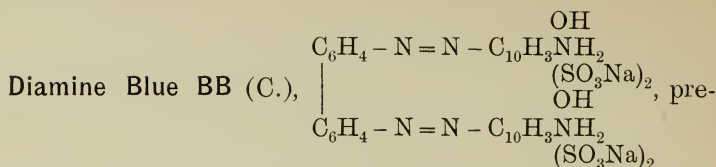
Consequently, Dianisidine Blue is insoluble in water, and as such cannot be employed direct for dyeing, but has to be produced upon the fibre (see Nitraniline Red). This is effected according to a method introduced by the Höchst Farbwerke, wherein copper salts are used, and whereby dyeings are obtained that are distinguished by their indigo shade. Dianisidine Blue seemed destined to play an important part in calico printing ; but in consequence of its inability to resist the action of acids, these expectations have been only partially fulfilled.

Mention may here be made of a black developing dye that is produced from benzidine, dianisidine and β -naphthol. The mixture of these two bases is put on the market under the name of Azo Black Base O (M. L. Br.).

By employing peri derivatives as components, pure blue benzidine dye-stuffs have at length been obtained, 1. 8. dioxynaphthalene- and amidonaphthol-4.-sulphonic acid, as also 1. 8. amidonaphthol-3. 6. and -2. 4.-disulphonic acid, having proved especially valuable in this connection. Several of the dye-stuffs prepared in this manner give more handsome shades when benzoylated. Great importance attaches to 2. 8. amidonaphthol-6.-sulphonic acid, coupled in an alkaline solution, for black dye-stuffs. When coupled in acid solution it gives violet dye-stuffs, fast to light, like diamine violet (C.). The following may serve as examples :—



dianisidine and 1. 8. dioxynaphthalene-4.-sulphonic acid.



pared by coupling tetrazotised benzidine with 2 molecules of 1. 8. amidonaphthol-3. 6.-disulphonic acid in alkaline solution.

Diamine Pure Blue (C.) is produced in the same way from dianisidine and the same amidonaphtholsulphonic acid. It is distinguished by its particularly pure blue dyeings, and is identical with Benzo Pure Blue (By.) and Congo Pure Blue (Act.).

The handsomest and clearest blue dye-stuff of this group is **Chicago Blue 6B** (Act.), **Brilliant Benzol Blue 6B** (By.), **Diamine Pure Blue FF** (C.), prepared from dianisidine and 1. 8. amidonaphthol-2. 4.-disulphonic acid.

A larger number of identical blue dye-stuffs are met with in commerce under the names Benzo Blue, Diamine Blue, Benzo Cyanine, Diamine Cyanine, Congo Blue, Congo Cyanine, Chicago Blue and Columbia Blue. These are tetrazo dye-stuffs from toluidine or dianisidine and 1. 8. amidonaphthol-4.-sulphonic acid, or mixed periamidonaphtholsulphonic acid dye-stuffs, mostly prepared with 1. 8. amidonaphthol-4.- and 2. 4.-disulphonic acids. They belong to the so-called "Blue Convention".

In this latter category are comprised the following: Benzo Blue 3B, 2B and BX, identical with Congo Blue 3B, 2BX, BX and Diamine Blue 3B, 2B, BX; Benzo Blue 2R, 4R, RW, identical with Chicago Blue 2R, 4R, RW, and Diamine Blue C2R, C4R, RW; Chicago Blue B, R, identical with Diamine Blue CB, CR; Chicago Blue 6B, identical with Brilliant Benzo Blue 6B and Diamine Pure Blue FF; Benzo Pure Blue (concentrated), identical with Congo Pure Blue and Diamine Pure Blue; Benzo Pure Blue, identical

with Congo Pure Blue A and Diamine Pure Blue A ; Benzo Pure Blue 4B, identical with Chicago Blue 4B and Diamine Blue C4B ; Benzocyanine 3B, B, R, identical with the corresponding marks of Congo Cyanine and Diamine Cyanine ; Benzo Red-blue G, R, identical with Columbia Blue G, R, and Diamine Blue LG, LR.

To this group (though not to the Blue Convention) belong also the following dye-stuffs : Dianile Blue R and B (M. L. Br.), from benzidine (or toluidine and dianisidine) and chromotropic acid ; Diamine Brilliant Blue (C.), from dianisidine, 1. 8. chloronaphthol-3. 6.-disulphonic acid and naphtholsulphonic acid ; Oxamine Blue and Oxamine Violet (B.), produced by the aid of amidonaphthol-7.-sulphonic acid ; the Oehler dye-stuffs, Azo Mauve, Azo Black-blue, Naphthazurine, etc.

The production of dye-stuffs from amidonaphtholsulphonic acids has led to the introduction of an important technical innovation, which consists in the conversion of these dye-stuffs into complex azo compounds on the (cotton) fibre.

The resulting dye is fixed in the following manner : The dyed cotton is treated in a second bath with sodium nitrite and hydrochloric acid, and then transferred to the so-called "developing bath," wherein the diazo compound is combined with a phenol or amine, these latter being termed "developers".

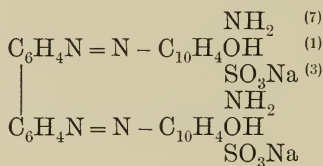
These dyes, when thus "developed on the fibre," are deeper in colour, and mostly faster than those obtained in the first bath. (This usually applies solely to the washing fastness, and not the fastness to light.)

The oldest dye-stuff of this group is the **Diamine Black RO**,* introduced by L. Cassella & Co.

* The mark BO is prepared with ethoxybenzidine, instead of benzidine, the mark BH (identical with Bayer's Diazo Black BHN) from benzidine, 2. 8. amidonaphthol-6.-sulphonic acid and 1. 8. amidonaphthol-3. 6.-disulphonic acid.

For using this dye-stuff the method first introduced by the Farbenfabriken, form. Fr. Bayer & Co., for Primuline (*q.v.*) has been elaborated to such an extent that at present large quantities of cotton are dyed with this and similar dye-stuffs.

It is produced by the action of 2 molecules of amidonaphtholsulphonic acid G $\left(\text{NH}_2 \text{C}_{10}\text{H}_7\text{SO}_2\text{Na} \right)$ on diazotised benzidine :



The coupling must be effected in an alkaline solution, a different dye-stuff, *viz.*, **Diamine Violet N (C.)**, being obtained when an acid solution is employed.

In place of amidonaphtholsulphonic acid other isomers or similar compounds are used for the preparation of dye-stuffs of this kind, special preference being accorded to the sulpho derivatives of amidonaphthol 1. 8.

Of the various Diamine Blacks, or Diazo Blacks, the mark BH is the one mostly used as a diazotising dye-stuff.

A large number of these dye-stuffs, diazotisable on the fibre, are met with in commerce under a variety of names ; some of them, however, belong to the triazo dye-stuffs, and to classes derived from bases other than benzidine. Dark blue and brown colours are also produced by diazotisation on the fibre.

These dye-stuffs also yield useful dyeings by themselves, but for the most part they are diazotised and developed. The developers used comprise: β -naphthol, m. phenylenediamine, naphthylamine ether, amidodiphenylamine (Cas-

sella's developer AD), amidonaphtholsulphonic acids, etc.* Some of the colours obtained by direct dyeing are entirely altered by diazotising and developing, the blue produced by Benzo Blue (By.), for instance, being turned grey by diazotising and developing. Sometimes, after diazotising, a treatment with soda is given, instead of developing, whereby the diazotised amido group is apparently exchanged for hydroxyl; this may be done in the case of Columbia Black, Diazo Brilliant Black, etc.† The last-named dye-stuff, for example, gives a dirty red when used direct; but this is changed into a handsome catechu brown by diazotisation and treatment with soda.

POLYAZO DYE-STUFFS FROM BENZIDINE BASES.

The same products as those described above are also sold in the finished state as polyazo dyes. In their preparation use is generally made of the property of tetrazotised benzidine bases of forming an intermediate product with 1 molecule of an azo component. Thus, for example, when α -naphthylamine is allowed to act on tetrazotised benzidine, the

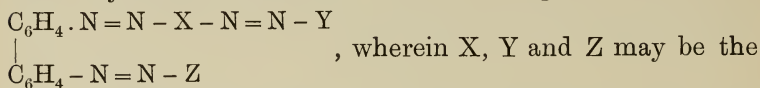
substance
$$\begin{array}{c} \text{C}_6\text{H}_4 - \text{N} = \text{N} - \text{C}_{10}\text{H}_6\text{NH}_2 \\ | \\ \text{C}_6\text{H}_4 - \text{N} = \text{N} - \text{Cl} \end{array}$$
 is generally obtained as

the first product. On then diazotising the NH_2 group of the naphthylamine therein there are formed two free diazo groups, which can be combined with different azo components. The above substance, for example, furnishes under this treatment with 2 molecules of 1. 8. dioxynaphthalene-4.-sulphonic acid a blue dye-stuff—Benzoinidigo Blue (By.)—and with 2 molecules of 1. 6. amidonaphthol-3.-disulphonic acid a greenish-blue dye—Diazo Blue-black (By.).

* Blue developer AN (C.), for example, is amido- β -naphtholsulphonic acid G.

† The mark B (By.) of this dye-stuff is prepared from dianisidine and 2 molecules of 1. 6. naphthylaminesulphonic acid.

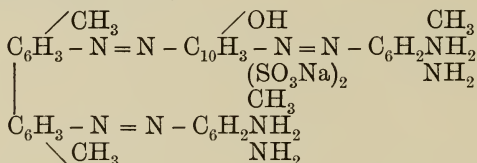
Very frequently 2. 8. amidonaphthol-6.-sulphonic acid is used instead of *a*-naphthylamine as intermediate link. Such dye-stuffs therefore exhibit the general formula :



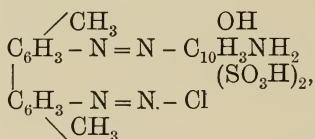
same or different bodies. Of course, benzidine can be replaced by other similar bases, such as toluidine, dianisidine, etc.

The following dye-stuffs may be cited as examples :—

Columbia Black (Act.),

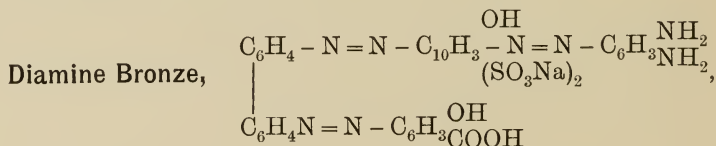


This is prepared by first combining tetrazotised toluidine with 1 molecule of 2. 8. amidonaphthol-3. 6.-disulphonic acid to form the intermediate product,



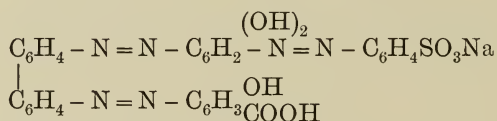
the NH_2 group of the amidonaphtholsulphonic acid being then diazotised, and the resulting substance coupled with 1 molecule of m. toluylenediamine.

The mark B of this Columbia Black was the first substantive cotton dye-stuff to furnish a deep black direct (*i.e.*, without further development on the fibre).



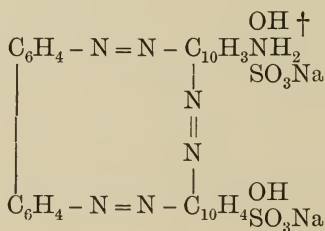
from benzidine, 1. 8. amidonaphthol-3. 6.-disulphonic acid,

component) with chrysoidine or with a resorcine monoazo dye-stuff. They are, however, for the most part preferably prepared in such a way that the said monoazo dye-stuff is applied in an unfinished state, *viz.*, by coupling tetrazotised benzidine (for instance) with salicylic acid and resorcine, and then allowing a diazo compound to react on the resulting tetrazo dye-stuff. The latter enters the resorcine nucleus. On employing sulphanilic acid or naphthionic acid as the diazo compound in this instance, the product known as **Congo Brown G and B (Act.)** is obtained.



These dye-stuffs are also partly produced on the fibre by introducing the final component as a diazo compound into the molecule of the dye-stuff after dyeing. Of this kind are the Benzonitrol dyes (By.), Dianile Black (M. L. Br.), Diamine-Nitrazol Black (C.),* etc., the dyeings of which are developed by means of p. nitraniline.

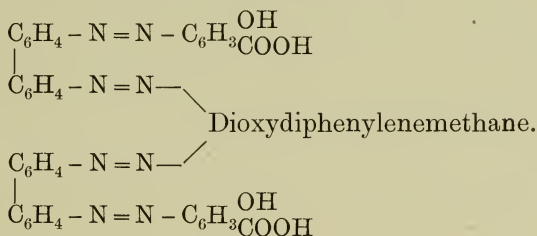
In the development of monoazo dye-stuffs on tetrazotised benzidine bases it has been found that, in some cases, only 1 molecule of the former is needed to completely satisfy the tetrazotised base. It is assumed that, in such case (when benzidine is used), an atomic complex of the following form is produced:—



* A mixture.

† According to the German Patent, No. 86,198, of Kalle & Co.

Finally, mention may be here made of the benzidine dye-stuffs prepared by means of dioxydiphenylmethane. These are obtained by the action of 2 molecules of the intermediate product from tetrazotised benzidine and an azo component on 1 molecule of dioxydiphenylmethane. The **Mekong Yellow** (DH) belonging to this class, and prepared from benzidine, salicylic acid and dioxydiphenylmethane, has, therefore, the following composition :—



Of the benzidine dye-stuffs containing only a single azo group, mention should be made of **Diamond Flavine** (By.),



This is prepared by allowing 1 molecule of salicylic acid to act on diazotised benzidine, and replacing the free diazo group in the resulting product with hydroxyl (by boiling with water).

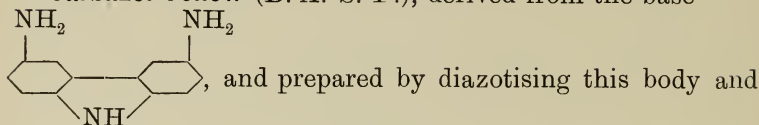
Although this dye-stuff is not altogether incapable of dyeing unmordanted cotton, it is really only suitable for dyeing chrome-mordanted wool. The dyeings form a cheap substitute for fustic, and are also faster to light than this latter.

To the same category belongs Pick & Lange's **Dutch Yellow** (no longer in the market), which was prepared by the action of sulphite on the intermediate product from tetrazotised benzidine and salicylic acid; also a blue dye-stuff (Steiner's French Patent, 285,456, 1899) obtained by boiling the intermediate product from tetrazotised benzidine and 1 molecule of 1. 8. amidonaphthol-3. 6.-disulphonic acid.

DYE SALTS DERIVED FROM OTHER BASES.

To these belong :—

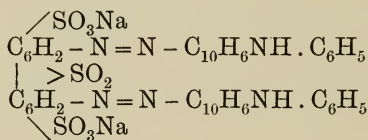
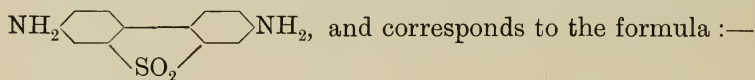
Carbazol Yellow (B. A. S. F.), derived from the base



coupling it with 2 molecules of salicylic acid. It is a mordant dye-stuff, and its chrome lake can be used for all three fibres.

p. Diamidodimethylcarbazol gives with β -naphthol a black, which is sold, as a developing (ice) dye, under the name Azophore Black (M. L. Br.).

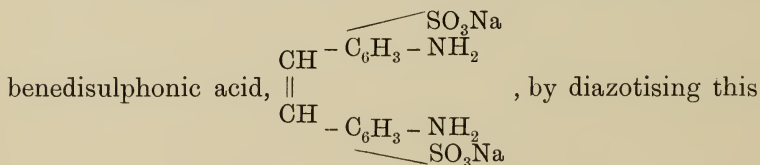
Sulphonazurine (By.) is derived from benzidinesulphone,



It is prepared by the action of 2 molecules of phenyl- β -naphthylamine on diazotised benzidinesulphondisulphonic acid.

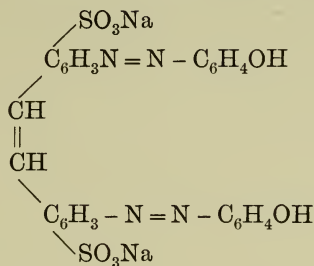
Both this dye-stuff and the allied Brilliant Sulphonazurine (By.) are more purely blue, and of greener tinge than Benzazurine ; they are better adapted for dyeing wool than cotton.

The “**stilbene dye-stuffs**” are derived from diamidostil-



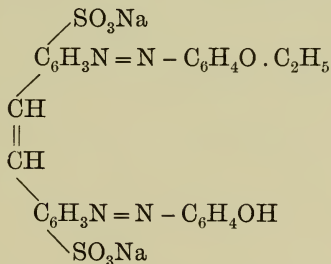
body and then allowing phenol, salicylic acid, naphthylaminesulphonic acids, etc., to react thereon.

Of this class is **Brilliant Yellow** (By., Leonh.):



a dye-stuff which is very fast to light, though sensitive to alkalis and copper. It is used for dyeing paper.

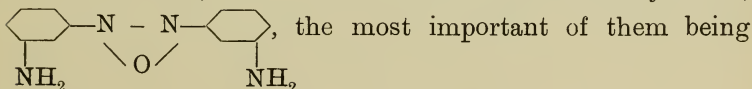
Chrysophenine is prepared by ethylating Brilliant Yellow, in which operation, according to Richard Meyer, only one hydroxyl group is substituted. Consequently its formula is:—

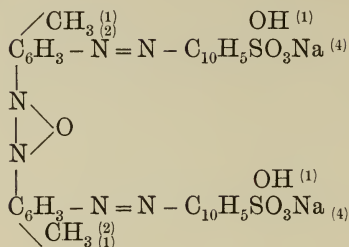


In contrast to Brilliant Yellow this dye-stuff is fast towards alkalis, and indeed is one of the most valuable and frequently used dye salts, being applicable to all textile fibres. The dyeings it furnishes are very fast in this respect.

Other members of the stilbene class are the “Hessian dye-stuffs” of A. Leonhardt & Co., *e.g.*, Hessian Yellow, Hessian Violet, Hessian Purple, etc.

Rosenstiehl and Noelting’s dye-stuffs (so-called after their inventors) are derived from diamidoazooxybenzol,



St. Denis Red :

This is applied to cotton in a different manner from the benzidine dye-stuffs, an addition of common salt and soda lye being made to the dye bath, and the goods being afterwards passed through sulphuric acid. These dyeings are better able to resist mineral acids than those furnished by the benzidine dyes.

Latterly St. Denis Red has also been put on the market under other names: Dianthine Red 4B (Read, Holliday & Sons), Rosophenine (Clayton Aniline Co.) and Trona Red (Bayer & Co.), and is used for dyeing bedtickings. Good blue dye-stuffs are prepared from amidoazooxybenzol with amidonaphtholsulphonic acids (*e.g.*, 1. 8. amidonaphthol-3. 6.-disulphonic acid).

Salmon Red and **Cotton Yellow G** (B. A. S. F.) are derived from a diamidodiphenylurea,

$$\begin{array}{c}
 \diagup \text{NH} \cdot \text{C}_6\text{H}_4\text{NH}_2 \\
 \text{CO} \\
 \diagdown \text{NH} \cdot \text{C}_6\text{H}_4\text{NH}_2
 \end{array}$$

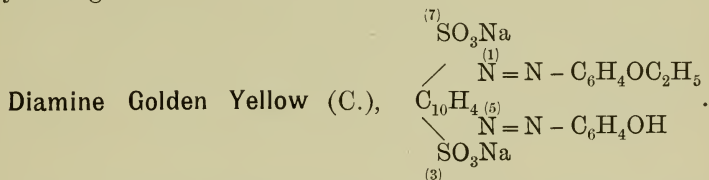
In the former case naphthionic acid, and in the other salicylic acid, is used as the second component.

Heligoland Yellow (Noetzel) is prepared from diamido-diphenylthiurea, phenol and salicylic acid.

DYE-STUFFS DERIVED FROM NAPHTHYLENEDIAMINES.

Dye-stuffs of this kind—which, however, are not dye salts—we have already become acquainted with in the tetrazo dye-stuff group (see Naphthol Black). It was there stated that salt dye-stuffs can be prepared by using special

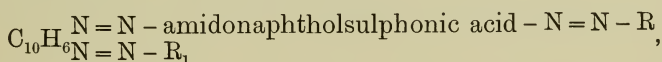
components, *e.g.*, 2. amido-5.-naphthol-7.-sulphonic acid. For the direct preparation of these dye-stuffs with suitable azo components, use is made of the naphthylenediamines 1. 5. and 1. 4. Thus 1. 5. naphthylenediamine-3. 7.-disulphonic acid combined with 2 molecules of phenol and afterwards ethylated gives



According to Richard Meyer only one hydroxyl group reacts during ethylation—just as in the case of chrysophenine already mentioned.

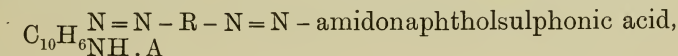
On account of the readiness with which it can be discharged Diamine Golden Yellow is largely used in printing.

By employing some component susceptible of further diazotisation, *e.g.*, an amidonaphtholsulphonic acid, it is possible to obtain dye-stuffs analogous to Diamine Bronze in composition. For instance :—



wherein R and R₁ may be any suitable azo components.

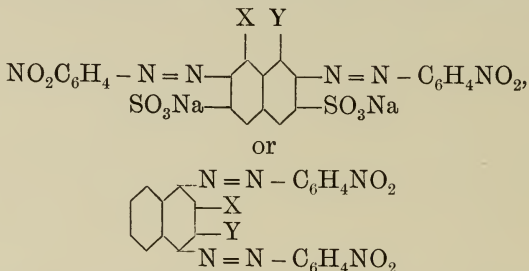
1-4 naphthylenediamine and its sulpho acids can also be used, diazotised in only one amido group, in the preparation of salt dyes. They correspond to the formula :—



R representing an azo component with one diazotisable amido group, and A the acetyl group.

To this class belong the **Diaminogenes** (C.), so highly appreciated on account of their fastness; of which series, Diaminogene Blue BB is similar to Bayer's Diazoindigo Blue.

Other dye-stuffs belonging to the same category are those prepared from 1. 8. or 2. 3. diamido-, amidooxy- or dioxynaphthalenesulphonic acids, in the following manner. The first step is to introduce 2 molecules of p. nitrodiazobenzol :

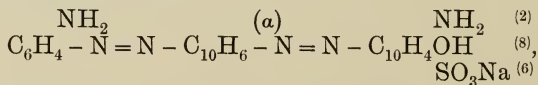


(OH or NH₂ groups take the place of X and Y) ; then the NO₂ is reduced to NH₂, and the product diazotised, and coupled with azo components. These dye-stuffs are black.

Of the diamines of the benzol series, use is made of p. phenylenediamine, m. phenylene- and toluenylenediamine, and sulpho acids, the latter for the production of salt dye-stuffs.

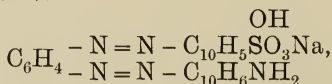
From paraphenylenediamine are derived both secondary diazo dye-stuffs, similar to Naphthol Black in composition, *e.g.* :—

Nyanza Black (Act.),



as also dye-stuffs analogous in composition to the benzidine dye-stuffs, *e.g.* :—

Violet Black (B.),



from p. phenylenediamine, 1. 4. naphtholsulphonic acid, and α-naphthylamine. This was the first of the black salt dye-stuffs.

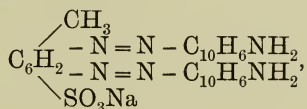
Columbia Black FF extra (Act.) must also be included in the group.

In a similar manner, p. diamidodiphenylamine and its monosulphonic acid are also used in the production of salt dyes. From these are derived various **Diamond Deep Blacks** (*e.g.*, SS) from Cassella & Co. and Bayer's **Pluto Black**.

A large number of (mostly brown) polyazo dye-stuffs are derived from metaphenylene- or toluylenediamine and their sulpho acids, the preparation of salt dye-stuffs therefrom being effected in various ways.

1. By diazotising the diamine and acting thereon with azo components. This treatment gives :—

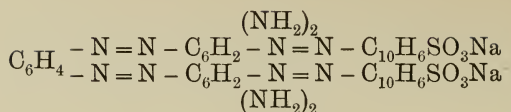
Tolulene Orange RR (Oe.),



from m. toluylenediaminesulphonic acid and 2 molecules of β -naphthylamine. If the latter be replaced by nitrometaphenylenediamine, the product is **Tolulene Yellow** (Oe.).

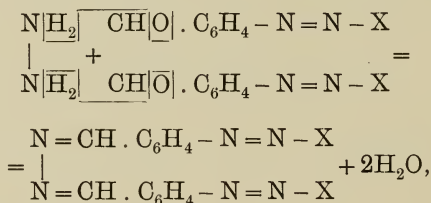
Tolulene Brown (Oe.) is obtained when only 1 molecule of m. phenylenediamine is allowed to act on tetrazotised m. toluylenediaminesulphonic acid.

2. Diazo compounds are allowed to act on the said metadiamines, or on azo dye-stuffs prepared therefrom (**Bismarck Brown**). The diazo compounds used in this case are mostly these of the benzol series (sulphanilic acid, m. amidobenzoic acid, etc.); *e.g.*, **Leather Brown** (O.), which is formed when p. phenylenediamine is acetylated singly, then diazotised, and (2 molecules) allowed to act on 1 molecule of m. phenylenediamine. **Benzo Brown B** (By.) results from the action of 2 molecules of diazonaphthionic acid on 1 molecule of **Bismarck Brown**. The presumptive composition of the dye-stuff is represented by the formula :—



To this class belong also several Hessian Browns (L.), Toluylene Brown, etc. Benzo Brown BX and BR, derivatives of Chrysoidine, are identical with Cotton Brown A and N (C.).

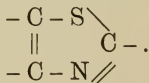
Finally, there are also salt dye-stuffs that are derived from simple diamine, $\begin{array}{c} \text{NH}_2 \\ | \\ \text{NH}_2 \end{array}$. They are obtained by allowing this body to act on azo dye-stuffs which contain an aldehyde group; their method of formation and composition can be represented as follows:—



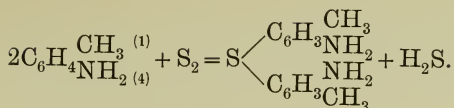
wherein X is an azo component.

THIAZOL DYE-STUFFS (PRIMULINE DYE-STUFFS).

The only property these dye-stuffs have in common with the substantive dye-stuffs already described is that of affinity for untanned cotton. In constitution they are very different, since they all contain the thiobenzol ring,



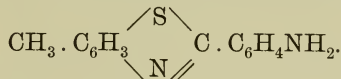
The action of sulphur on aromatic amines was first investigated by Merz and Weith. They heated, *e.g.*, p. toluidine along with sulphur to a temperature of 140° C., in presence of lead oxide, for combining with the liberated sulphuretted hydrogen, and obtained thiotoluidine:



Subsequently Dahl & Co. took out a patent for this reaction, but carried on at a higher temperature (175° C.) and without lead oxide; this furnishes a body containing four atoms of hydrogen less, and afterwards termed dehydrothiitoluidine. When the NH₂ group is eliminated therefrom there results a homologue of Hofmann's benzyl-

amidophenylmercaptan, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{S} \diagdown \\ \diagdown \text{N} \diagup \end{array} \text{C} \cdot \text{C}_6\text{H}_5$.

The composition of dehydrothiitoluidine is therefore :—



This compound is not a dye-stuff; but if a higher temperature and more sulphur be employed in its preparation there results a base which, on sulphonation, furnishes the first dye-stuff of this group, **Primuline Yellow**.

This was discovered in 1887 by Green, chemist to Messrs. Brooke, Simpson & Spiller, of London, and is prepared by bringing together several molecules of dehydrothiitoluidine.

Applied to cotton Primuline gives a very pure yellow, which, however, is of no practical value, owing to its very fugitive character when exposed to light. The aforesaid method of diazotising and developing the dye on the fibre was first applied to this dye-stuff, and the name "ingrain colours" was given to the dye-stuffs concerned. In this particular instance the diazo compound is very fugitive, and therefore if a piece of cotton dyed with Primuline be partly covered over and then exposed to light, the diazo compound in the uncovered portion will be entirely destroyed. On now treating the piece with a phenol (a developer) the covered portion alone will be dyed, *i.e.*,

coloured figures will be obtained. This process has been proposed for producing pictures.

The primuline dyes are fast to washing, but not to light. Practical importance, however, has been attained by Primuline Red (primuline dyeing developed with β -naphthol) and Primuline Bordeaux (developed with ethyl- β -naphthylamine).

Dye-stuffs identical with or very similar to Primuline in composition are sold under various names: Primuline (By., B.), Thiochromogene (Dahl), Polychromine (Geigy), Chromine (Kalle). This last-named differs from Primuline in being non-diazotisable.

Other dye-stuffs of the same group can be prepared from Primuline in various ways.

By diazotising and coupling with salicylic acid (or similar components) yellow dye-stuffs are produced, like Geigy's Orio Yellow, which is sold under the names Cotton Yellow R (B.) and Alkali Yellow (D.). It may also be fixed as a chrome lake on cotton, and is used in this manner in calico printing.

To the same class belongs also the valuable **Milling Yellow O** (C.), which is very suitable for dyeing wool.

Dianile Yellow (M. L. Br.) is obtained by coupling diazotised Primuline with acetoacetic ester.

A brown dye-stuff of this class put on the market by Dahl & Co. under the name **Alkali Brown** is produced by the action of phenylenediamine on diazotised primuline. With this is closely allied the Cotton Brown of the same makers, which is identical with R. Geigy's Terra Cotta.

Mimosa (Geigy) is a yellow dye-stuff prepared by acting upon diazotised Primuline with ammonia.

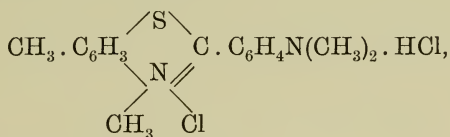
Yellow dye-stuffs characterised by great fastness towards light, and especially so towards chlorine, have been obtained by the action of hypochlorites on dehydrothiotoluidinesulphonic acid, or on Primuline and similar compounds.

Products of this kind, partly identical and partly of almost identical composition, are sold under the names Chloramine Yellow (By.), Oxyphenine (Cl. C.), Chlorophenine (Cl. C.), Fast Diamine Yellow B (C.), and Columbia Yellow (Act.). Other similar dye-stuffs are: Curcuphenine Yellow (Cl. C.), Nitrophenine (Cl. C.) and Chlorophenine Orange (Cl. C.).

The action of formaldehyde on Primuline furnishes a greenish yellow dye-stuff (Br. S. Sp.).

Other dye-stuffs of this group are the following :—

Thioflavine T (C.) is the methyl chloride compound of dimethyldehydrothiotoluidine :



and is a basic tannin dye-stuff.

Thioflavine S (C.) is the sodium salt of sulphonated dimethyldehydrothiotoluidine.

Thiazol Yellow (By.), Clayton Yellow (Cl. C.), and Turmerine (Br. S. Sp.), is formed by the action of dehydrothiotoluidinesulphonic acid on the diazo compound of the same acid. Its cotton dyeings are pure yellow, but fugitive to light and acids.

A number of red dye-stuffs of this group are formed by the action of azo components on the naphthalene series on diazotised dehydrothio bases; *e.g.*, **Erica** (Act.) from dehydrothioxylidine and an α -naphtholdisulphonic acid; Diamine Rose (C.) from dehydrothiotoluidine and 1. 8. chloronaphthol-3. 6.-disulphonic acid, etc.

Further dye-stuffs of this nature are :—

Geranine (By.), Brilliant Geranine (By.), Titan Rose (Br. S. Sp.), Patent Atlas Red (Br. S. Sp.), Emin Red (Act.), Columbia Red 8B (Act.), Direct Scarlet (K.), Thiazine Red (B.), Salmon Red (B.), Thiazine Brown (B.), etc.

Some of these dye-stuffs can also be fixed with mordants ; *e.g.*, Oriole Yellow with chrome on cotton ; Emin Red on wool.

Special mention must be made of the following :—

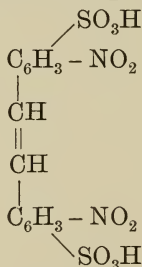
1. Thiazol Yellow and Thioflavine ; because they are the purest of all substantive yellows, and can, therefore, also be used in the production of greens.

2. Chloramine Yellow, Oriole Yellow and Milling Yellow, owing to their superior fastness to the others.

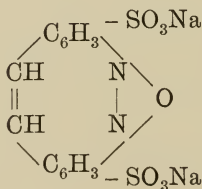
3. Erica, Geranine and Brilliant Geranine, which have attained a high position in practice for dyeing cotton pink ; as also Primuline for red ; on account of their fastness to washing.

AZOXYSTILBENE DYE-STUFFS.

This group comprises a number of yellow salt dyes derived from a dinitrostilbenedisulphonic acid,



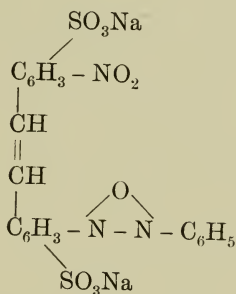
Curcumine S (Oe.), or **Sun Yellow** (Gg.), is formed when caustic alkalis are allowed to react on p. nitrotoluosulphonic acid. According to G. Schultz, they have the following constitution :—



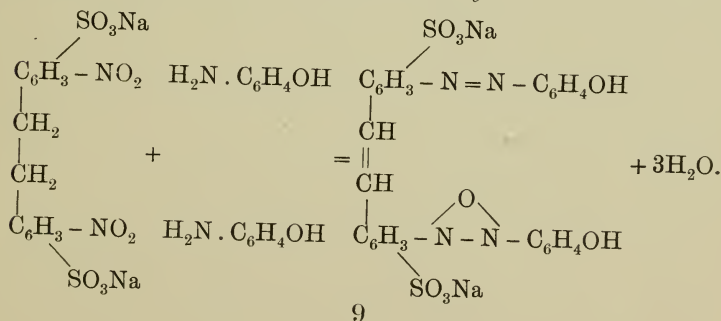
An analogous process results in the formation of **Direct Yellow** (K., By., Leonh.), which is probably the sodium salt of nitrostilbenedisulphonic acid. By reduction, this furnishes **Direct Orange** (K.); and by oxidation a yellow dye-stuff is obtained.

The foregoing reaction: the working of caustic alkalis on p. nitrotoluolsulphonic acid can also be performed in presence of aromatic bases or dehydrothio bases (*e.g.*, Primuline).

Dye-stuffs are also obtained in a similar manner from dinitrostilbenedisulphonic acid itself. In the condensation of this acid with amines, either 1 or 2 molecules of the latter may come into action, the result (according to the patent specification) being azoxy compounds, *e.g.*, by condensation with aniline:—



Dinitrobenzyldisulphonic acid also can be condensed with amines in presence of alkalis, oxidation to a stilbene derivative also occurring at the same time, *e.g.*:—



The resulting dye-stuff is therefore regarded as an azo-oxyazo compound.

To this class of dye-stuffs also belong the **Mikado dyes** of A. Leonhardt & Co. Mikado Yellow is identical with the above-mentioned Direct Yellow (K.). Leonhardt's Mikado Orange is also sold by Fr. Bayer & Co. under the name of Chloramine Orange.

The application of the Mikado dyes differs from that of the other salt dye-stuffs, inasmuch as a considerable addition of common salt is essential. Hence they are very fast to washing, the tendency of the colour to run into any adjacent white threads being very slight.

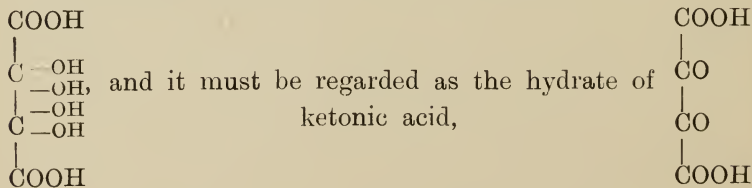
A few of these dyes are better suited for dyeing animal fibres.

As an entirely new class of red dye-stuffs which are apparently derived from dinaphthylamine may be mentioned **Benzorhoduline Red**, and the Benzo Fast Scarlet and Benzo Fast Red (Bayer & Co.) derived from carbamides of 2. 5. 7. amidonaphtholsulphonic acid.

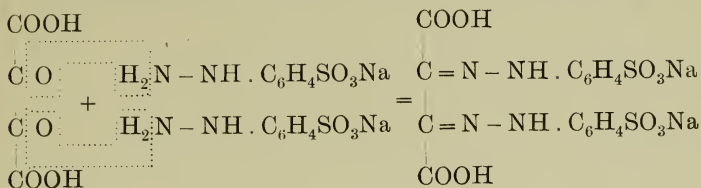
Other substantive cotton dye-stuffs, such as Rhodamine S, cannot be dealt with in this place.

HYDRAZONES.

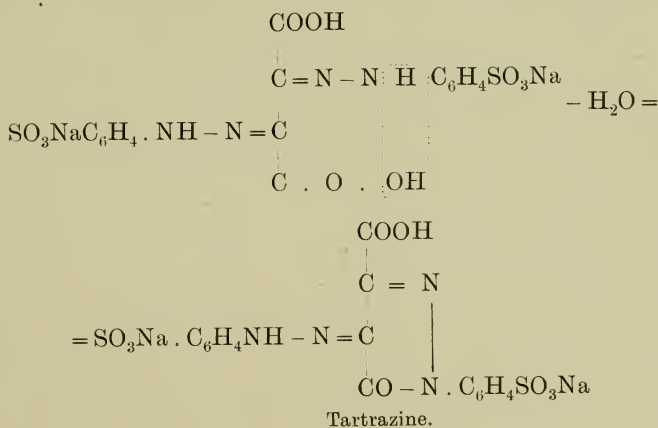
By the action of phenylhydrazinesulphonic acid on a solution of sodium dioxytartrate, Ziegler, in 1884, obtained a yellow dye-stuff, which, under the name **Tartrazine**, was introduced into commerce by the Badische Anilin- und Sodafabrik. The formula attributed to dioxytartaric acid in its hydrated condition, is the following:—



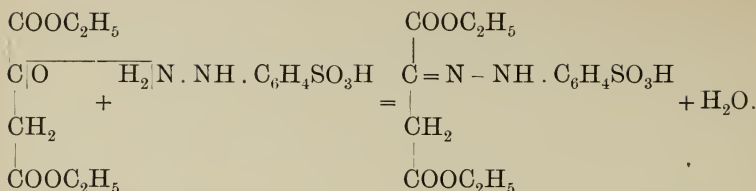
On the basis of this formula the origin and constitution of Tartrazine may be expressed by the following equation :—



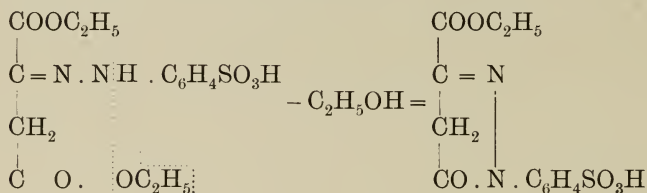
More recent researches by Anschütz have, however, shown that a substance of this composition merely occurs as an intermediate product in the preparation of Tartrazine. There ensues elimination of water between a carboxyl group and a hydrazine group whereby a pyrazolone ring is formed. Consequently Tartrazine is a pyrazolone derivative :—



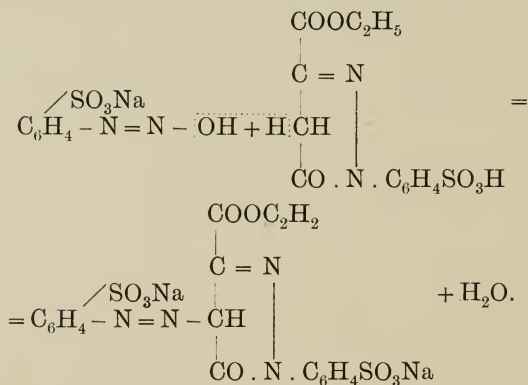
Another less advantageous but theoretically interesting method of preparing Tartrazine is that from oxalacetic ester. This method was discovered by Ziegler, and has latterly been improved by Anschütz and the Badische Anilin- und Sodafabrik. It consists in condensing oxalacetic ester with 1 molecule of phenylhydrazinesulphonic acid :



The resulting compound will decompose spontaneously—though the reaction is facilitated by heating—with elimination of alcohol, into a pyrazolone.



The sodium compound of this pyrazolone then furnishes with diazosulphanilic acid an ester of tartrazine :



Tartrazine is a very handsome yellow dye-stuff, extremely fast to light; of the other yellow dye-stuffs, only one, *viz.*, Fast Yellow (sodium amidoazobenzoldisulphonate), is superior in this respect. Consequently, Tartrazine plays a great part in wool dyeing.

The patent having expired, this dye is now also manufactured by other firms (By., M. L. Br.). One remarkable

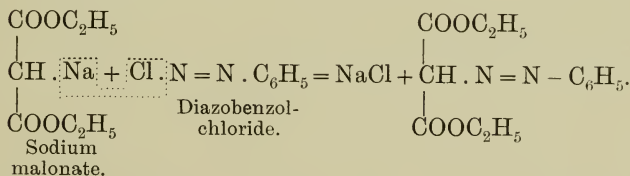
feature about the dye is its low fastness on silk ; for cotton it has no affinity at all. Tartrazine is the sole hydrazone dye-stuff of any technical importance.

Other dye-stuffs belonging hereto have been prepared and patented : from benzyl (and also phenanthraquinone) and aromatic hydrazines by R. Meyer ; and from hydrazines of aromatic amidocarbonic acids and dioxytartaric acid by Fr. Bayer & Co. In the same category is the Nitrazine Yellow (now no longer in the market) prepared by Oehler from dioxytartaric acid and nitroxylhydrazinesulphonic acid.

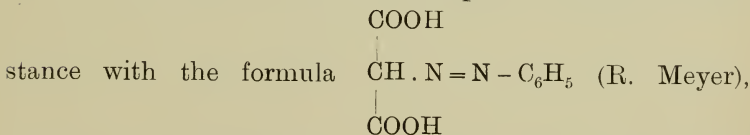
As is the case with the azo dye-stuffs, the problem of the constitution of the hydrazones cannot yet be definitely answered, opinions wavering, here also, between the hydrazone and the azo form, as expressed in the formulæ given below :—



In fact, certain newly discovered reactions furnish true azo compounds where the products should be hydrazones, and *vice versa*.

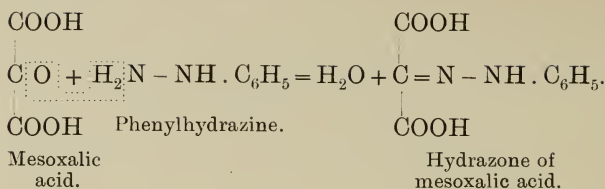


On saponification, the latter compound furnishes a sub-



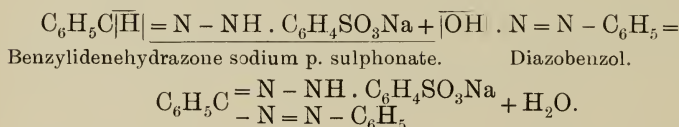
which is identical with the hydrazone of mesoxalic acid* prepared by E. Fischer and Elbers :—

* R. Meyer, *Berl. Ber.*, 1888, **21**, 118; 1891, **24**, 1243; Fischer and Elbers, *Ann. Chim.*, 1885, **227**, 355.



Similar cases are reported by Bernthsen,* Japp and Klingemann.†

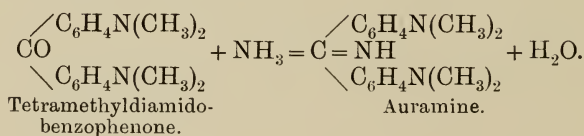
Mention may also be made in this place of the formazile compounds prepared by Pechmann‡ (from malonic acid, hydrazone and diazobenzol), and by E. Bamberger§ (from aceto-acetic ester and 2 molecules of diazobenzol), since their sulpho acids are dye-stuffs, *e.g.* :—



The compound thus formed acts as a red dye on wool. ||

KETONIMIDES.

In 1884 Caro and Kern, by fusing tetramethyldiamido-benzophenone with sal ammoniac in presence of zinc chloride, obtained a yellow dye-stuff, which was put on the market by the Badische Anilin- und Sodafabrik under the name **Auramine**. Its origin and constitution can be represented by the equation :—



* *Berl. Ber.*, 1888, **21**, 743.

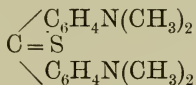
† *Ann. Chim.*, 1888, **247**, 190. See also Claisen and Beyer, *Berl. Ber.*, 1888, **21**, 1697.

‡ *Berl. Ber.*, **25**, 3175.

§ *Ibid.*, **25**, 3201.

|| *Fr. Fichter and Em. Schiess, Berl. Ber.*, **23**, 747.

At present this substance is prepared by the Sandmeyer method, *viz.*, heating tetramethyldiamidodiphenylmethane with sulphur, sal ammoniac and common salt in a current of ammonia gas. In this reaction thioketone,



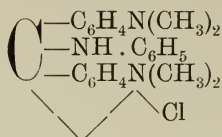
is formed as an intermediate product.

Auramine is a basic dye-stuff, and is met with in commerce as a hydrochloric salt. When first introduced it gave rise to the hope that it would fill a want, and play an important part in cotton dyeing and calico printing, as a basic tannin dye-stuff. These expectations, however, have not been altogether fulfilled, the dye lacking the fastness requisite for calico printing; and it also has the disadvantage of being readily decomposed by hot water. Nevertheless it is still the most largely used of all the yellow basic dye-stuffs, being of considerable importance as a constituent of mixed dyes for cotton, as well as for wool dyeings to resist sulphur, and for paper staining. In addition, it is employed for mixing with various dyes (*e.g.*, Fuchsine), and medicinally as "pyoctanine aureum," as a preventive of malignant new growths.

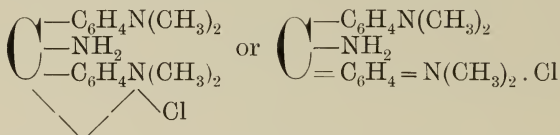
The auramines or ketonimide dye-stuffs are nearly allied in constitution to the triphenylmethane dye-stuffs to be described later on, these latter bodies being obtained when leucauramine (from the reduction of Auramine) is condensed with aromatic amines.

A similar result is obtained by the condensation of Auramine with phenols and oxycarbonic acids. This resemblance is intensified by the recent detection of an indigo group in phenylauramine by A. Stock,* which latter body as a chloride therefore has the composition:—

* *Journ. f. prakt. Chem.*, **47**, 401-413 (1893).



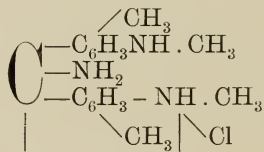
Consequently the composition of auramine chloride must be expressed by the formula,



which leaves the Auramine to appear as a derivative of triphenylmethane wherein one of the benzol nuclei is replaced by NH_2 . According to Hantzsch, the electrical behaviour of Auramine also harmonises with this conception of its constitution.

If, instead of the amido group, another amido radicle be introduced into Auramine, the colour of the resulting Auramine depends, according to Stock, on the basicity of this radicle: when this is very strongly basic the colour is yellow, but as the basicity diminishes it passes through yellowish-red into red; whilst if an acid radicle be introduced a violet-brown dye-stuff is produced.

A more greenish-yellow dye-stuff, named Auramine G,



is prepared from dimethylditoluylmethane. This latter is formed by the condensation of monomethyl-o.-toluidine with formaldehyde.

TRIPHENYLMETHANE DYE-STUFFS.

It was noticed by Nathanson in 1856 and by A. W. Hofmann, Roquencourt and Dorot in 1858, that under certain circumstances, aniline also furnished a red dye-stuff. Shortly afterwards (1859) Prof. Verguin of Lyons made the discovery that a red dye-stuff is formed when aniline is oxidised with tin chloride. This product he named Fuchsine, and began to manufacture the same in conjunction with the firm of Renard Brothers, silk dyers in Lyons.

This discovery was one of the most important ever made in the domain of chemical technology, since from it resulted the extraordinarily rapid development of the now so extensive industry of the artificial dye-stuffs.

Everyone turned to this valuable reaction, so that very soon a whole series of other oxidising agents for the production of Fuchsine were patented, chief among them being Brooman's mercury chloride process (1859) ; Medlock (1860), Nicholson, and Gerard and De Laire with arsenic acid ; Lauth, Laurent, Castelhaus and Coupier with nitrobenzol, etc.

Concurrently with these technological researches proceeded numerous scientific investigations on the part of A. W. Hofmann, Otto and Emil Fischer, Rosenstiehl, Doebner, Caro, Dale, Schorlemmer and others, which gradually elucidated not only the constitution of Fuchsine but also the mechanism of the formative process.

The first fundamental researches with regard to Fuchsine were those of A. W. Hofmann. He found this substance to be the salt of a base to which he gave the name rosaniline, which by reduction is converted into leucaniline, a body that, unlike rosaniline, does not furnish dye-stuffs with acids.

Despite numerous experiments, the constitution of Fuchsine long remained problematical. Attempts were made to

express this by various formulæ, of which that of Zulkowski (1869),* assuming the existence of three amido groups in the molecule of rosaniline, came nearest the truth.

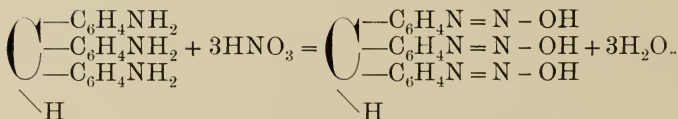
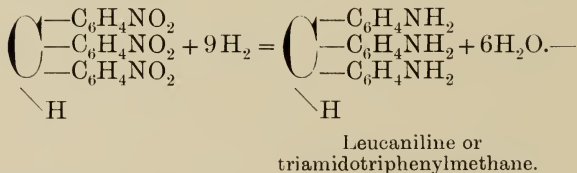
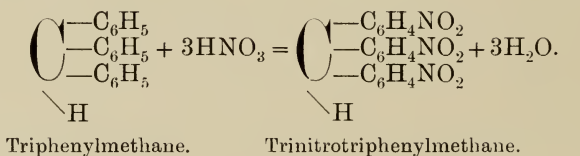
The successful elucidation of the constitution of Fuchsine we owe to the labours of Otto and Emil Fischer. These workers demonstrated that leucaniline is a primary triamine, which, on treatment with nitrous acid and subsequent boiling with absolute alcohol, undergoes conversion into triphenyl-

methane, $\text{C} \begin{array}{c} \text{---C}_6\text{H}_5 \\ \text{---C}_6\text{H}_5 \\ \text{---C}_6\text{H}_5 \\ \diagdown \\ \text{H} \end{array}$. They thereupon treated the product

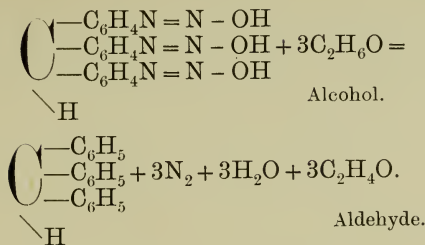
with fuming nitric acid, and thus obtained trinitrotriphenylmethane, which was transformed into leucaniline by reduction.

In this manner rosaniline was analytically and synthetically revealed as a derivative of triphenylmethane, and its constitution in the main elucidated.

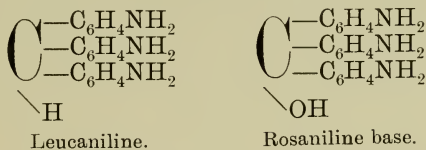
These two fundamental reactions can be expressed by the following equations :—



* *Sitzsber. d. kais. Akad.*, vol. 59; *Berl. Ber.*, 1876, **9**, 107.

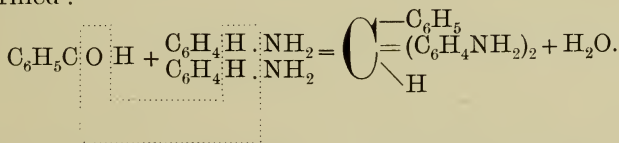


Consequently, leucaniline is a triamidotriphenylmethane, whereas the rosaniline base obtained therefrom by oxidation is regarded as a triamidotriphenylcarbinol:



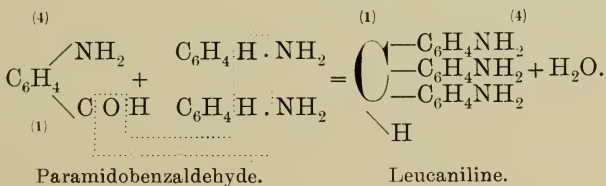
The further elucidation of the constitution of rosaniline necessitates the determination of the position occupied by the three amido groups in relation to the point of attachment with the methane carbon. This task is accomplished in the following manner:—

When benzaldehyde is condensed with aniline, by the aid of dehydrated zinc chloride, diamidotriphenylmethane is formed:—



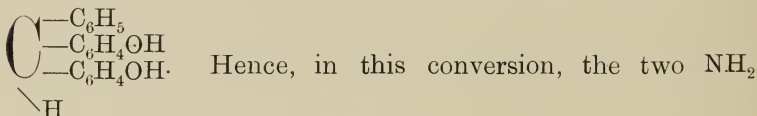
Benzaldehyde. 2 mol. aniline. Diamidotriphenylmethane.

If benzaldehyde be replaced by paramidobenzaldehyde, then the product is triamidotriphenylmethane or leucaniline:

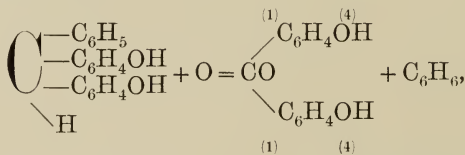


This synthesis proves that one NH_2 group of the leucaniline takes up the para position with regard to the point of attachment with the methane carbon. Moreover, this group is not one of those contained in the diamidotriphenylmethane, but the third one, which is first introduced into the molecule of the leucaniline by the employment of para-midobenzaldehyde. That the two amido groups of diamidotriphenylmethane also assume the para position with regard to the point of attachment of the methane carbon, can be demonstrated in the following manner:—

When diamidotriphenylmethane is treated with nitrous acid, there ensues a diazo derivative, which, when boiled with water, yields a dioxytriphenylmethane of the formula:—



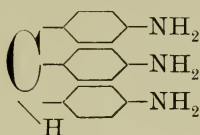
groups have merely been replaced by two OH groups, without any change of position having occurred. If, however, this dioxytriphenylmethane be fused along with caustic potash, there ensues addition of an atom of oxygen and elimination of benzol, resulting in the formation of dipara-dioxybenzophenone,



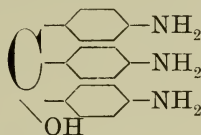
Dioxybenzophenone.

in which, as earlier researches had already shown, the two OH groups assume the para position to the ketone carbon—the former methane carbon in the dioxytriphenylmethane. This proves that the two OH groups of dioxytriphenylmethane, and also the two amido groups in the same sub-

stance, assume the para position towards the methane carbon. Consequently, the following constitutional formulæ apply to leucaniline and the rosaniline base respectively :—

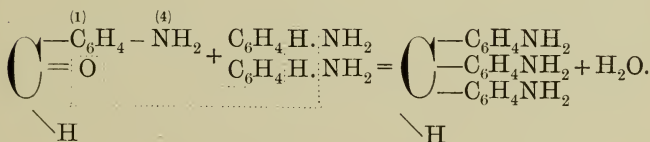
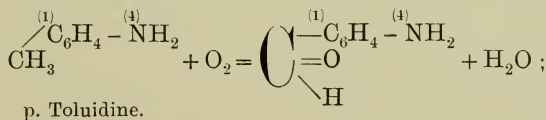


Leucaniline.

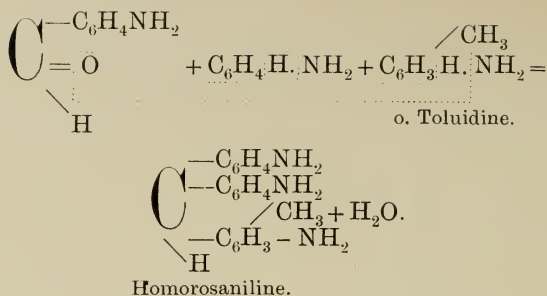


Rosaniline base.

A ready explanation is thus afforded of the fact, observed soon after the discovery of fuchsine, namely, that *pure* aniline does not furnish rosaniline when oxidised, but that the presence of paratoluidine is essential to this reaction, this last-named substance supplying from its methyl group the methane carbon necessary to the formation of a triphenylmethane derivative. In the production of rosaniline by the oxidation of impure aniline (containing paratoluidine), it is assumed that an aldehyde group is formed from the CH_3 group of the paratoluidine, and that then, by elimination of the oxygen of this aldehyde group, and the combination of the said oxygen with an atom of hydrogen from each of the two molecules of aniline to form water, rosaniline, or its leuco compound, is produced :—



In practice, a mixture of aniline, para- and orthotoluidine is invariably used, the collaboration of the last-named always leading to the formation of a second rosaniline.



To distinguish it from the first, or so-called pararosaniline, this product has been named homorosaniline.*

From the foregoing elucidation of the process of formation of rosaniline, follows the fact—also demonstrated by experiment—that neither of the two isomers of p. toluidine, viz., ortho- and meta-toluidine, can furnish rosaniline when oxidised, whether by themselves or along with aniline; since neither of the amido groups stands, with relation to the carbon of the methyl group (the subsequent methane carbon), in the para position necessary for rosaniline to be produced. It may be further deduced that only such amines can take part in the formation of rosaniline as have at liberty the position in their molecule standing in the para relation to the amido group, since it is at this point that the combination with the methane carbon must occur. Consequently, paratoluidine cannot, when oxidised by itself, furnish rosaniline.

Rosenstiehl and Gerber divide the homologues of aniline into three classes, according to whether they furnish rosaniline on oxidation, or not:—

1. The para derivatives, which furnish rosaniline when oxidised along with aniline, but not by themselves.
2. Ortho derivatives ($\text{NH}_2 : \text{CH}_3$ in ortho); these furnish

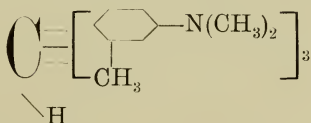
* The name pararosaniline was an arbitrary selection, and was not intended to denote the position of the amido groups, this relation not having been investigated at that time.

rosaniline when oxidised along with the bases of the first class, but not when oxidised alone or with aniline.

3. Meta derivatives ($\text{NH}_2:\text{CH}_3$ in meta); these bases do not furnish rosaniline on oxidation, whether alone or along with those of classes 1 and 2.

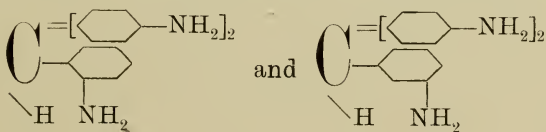
Hence, it is only when one of the CH_3 groups is in the meta position that a base becomes capable of taking part in the formation of rosaniline. An exception to this rule, however, is afforded by the bases of the foregoing class 1, wherein oxidation along with aniline results in the production of rosaniline on substitution taking place in the ortho or meta position; hence a para amine is always capable of this reaction.

The question now arises whether rosanilines in which the methyl group is in the meta position with regard to the amido group are actually capable of existing at all. This has been answered in the affirmative by the very comprehensive investigations of E. Noelting, who showed that it is possible to prepare, though not in the ordinary manner, rosanilines containing a CH_3 group in the meta position towards the amido group—not merely in one of the benzol nuclei, but in two or even all three. Thus the base

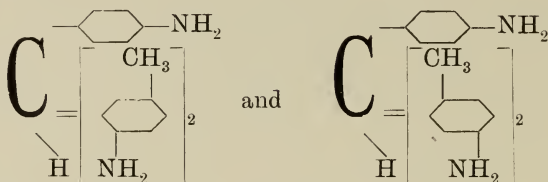


furnishes a blue rosaniline dye-stuff on oxidation.

Noelting has also shown that, by employing other means, it is also possible to obtain rosanilines which do not contain all the amido groups in para position with regard to the methane carbon. For instance, the leuco bases



furnish rosaniline dye-stuffs when oxidised. On the other hand, such bases as contain only one amido group in the para position and the other two in the ortho or meta position, *e.g.*,



do not give dye-stuffs on oxidation.

Rosanilines containing none of the three amido groups in the para position towards the methane carbon cannot be prepared at all.

Should one of the amido groups be lacking in rosaniline, the tinctorial character is not removed but only altered. The resulting substances—diamidotriphenylmethane dye-stuffs, or dye-stuffs of the Malachite Green series, as they are termed—are green to blue in colour. When one of the amido groups in rosaniline is acetylated, or converted into a quinoline group or an ammonium group, the effect is just as though it had been eliminated altogether, green dye-stuffs being produced. The same thing happens when the amido group is displaced by a sulpho group.

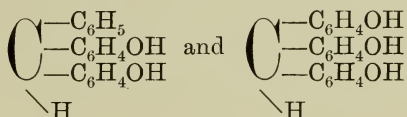
If, however, it be displaced by a hydroxyl group no important alteration of the colour ensues; and in fact all three amido groups can be displaced by hydroxyl without the tinctorial character being lost, though it disappears when all three amido groups are acetylated or converted into quinoline groups.

These facts, ascertained by Noelting, illustrate in a very decided and beautiful manner the important part played by the amido and hydroxyl groups as “auxochrome groups” (see Introduction).

Should two amido groups be lacking in rosaniline, there results paramonamidotriphenylmethane, the salts of which are orange coloured and will not dye either wool or silk, but only tanned cotton. In the isomeric metamonamidotriphenylmethane the tinctorial character is entirely wanting, and its salts are colourless.

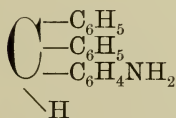
Hence the tinctorial character of rosaniline depends both on the number and position of the amido groups.

If the amido groups in diamido- and triamidotriphenylmethane be replaced by hydroxyl, there result dioxy- and trioxytriphenylmethane derivatives:—

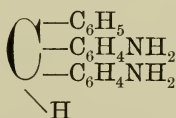


These substances and their derivatives form the group of the rosolic acid dye-stuffs. Rosolic acid has been obtained by diazotising homorosaniline and boiling the resulting diazo compound (Wanklyn and Caro); and the converse operation of converting rosolic acid into rosaniline has also been performed, by subjecting it to the action of ammonia under pressure (Dale and Schorlemmer). Hence in the rosolic acid dye-stuffs the hydroxyls occupy the same position towards the methane carbon as the amido groups do in rosaniline.

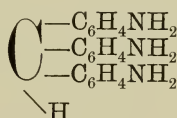
TYPICAL REPRESENTATIVES OF THE TRIPHENYLMETHANE DYE-STUFFS.



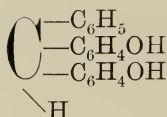
Monamidotriphenylmethane.
Incapable of furnishing dye-stuffs.



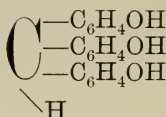
Diamidotriphenylmethane.
Leuco base of the Malachite Green group.



Triamidotriphenylmethane.
Leuco base of para-rosaniline.



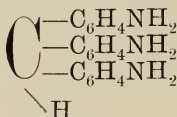
Dioxytriphenylmethane.



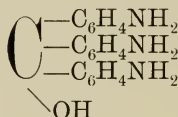
Trioxytriphenylmethane.

Fundamental substances of the rosolic acid dye-stuffs.

Leuco base, Rosaniline base and Hydrochloride.—As already stated, the rosaniline dye-stuffs are salts (usually chlorides) of bases which are converted into leuco bases by reduction. These are incapable of furnishing dye-stuffs with acids, but they may be retransformed by oxidation into the chromogenic bases, which latter are regarded as carbinols :—

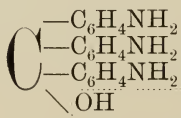


Leuco base.

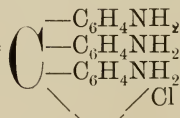


Carbinol base (rosaniline base).

On treating the carbinol base with an acid, one molecule of water is eliminated at first, and a monochloride is formed, the di- and trichlorides being produced by prolonging the reaction. Latterly Rosenstiehl has succeeded in obtaining a rosaniline salt containing four atoms of chlorine (see below). The more acid taken up by rosaniline (and its derivatives behave in a similar manner) the nearer does the resulting salt approach the colourless condition, and consequently the lower its stability; and only the monochlorides are of any practical value as dye-stuffs.* The transformation of the perfectly colourless carbinol base into the coloured form, in the process of conversion into a salt, is explained by Fischer in the following manner :—

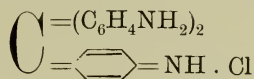


Rosaniline base.

Rosaniline chloride
(Fuchsine).

* Even these are in part hydrolysed by water.

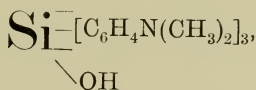
According to this assumption the formation of the salt takes place, with elimination of water, at one of the amido groups containing pentatomic nitrogen which is in direct combination with the methane carbon. Subsequently, on the basis of the newer formula for quinone, the formula for rosaniline chloride was remodelled by R. Nietzki as follows:—



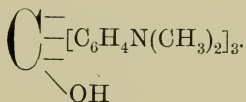
which is now used just as often as the original. In both the conversion of the colourless carbinol base into a dye-stuff by a constitutional modification is taken into account.

It is therefore assumed that the colour of Fuchsine is influenced by a “quinoid” linking, and the same hypothesis has also been applied to other rosaniline dye-stuffs, as well as to dye-stuffs of other groups. In all these cases the transition of a colourless base into a highly coloured dye salt is explained by the assumption of a constitutional modification, a transposition into a quinoid form.

An interesting contribution to this question was recently supplied by Combes, who prepared the silicon compound,

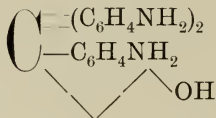


which is completely analogous in composition with a rosaniline derivative, the hexamethylrosaniline we shall describe later on,



However, whilst the latter is converted into a powerful dye by acids, the salts of Combes' base—in which apparently there is no quinoid linking—are quite colourless.

Such dye salts must be founded on bases of the quinoid type. For example, p. fuchsine must correspond to a colour base of the ammonium type, isomeric with the carbinol base :



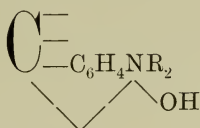
That coloured rosaniline bases actually exist was first demonstrated by the author in the case of p. fuchsine, and by Homolka in the case of New Fuchsine (see below), and that too in the following manner: If an aqueous solution of the said dye-stuff be treated with a slight excess of caustic soda in the cold a red precipitate is formed, which is completely soluble in ether, chloroform, etc., to an orange yellow liquid, from which the dye-stuff can be thrown down as a carbonate by the passage of a current of carbon dioxide.

The existence of a second rosaniline base was also subsequently demonstrated by Hantzsch and G. Osswald by electrical conductivity determinations. They found that the same is coloured, and dissociated by the strength of the potash and is therefore a true ammonium base; whereas the carbinol base is colourless and not dissociated—at least to any appreciable extent.

The carbinol base of Fuchsine is therefore incapable of direct conversion into salts. According to Hantzsch, it is a “pseudo base,” and in conversion into Fuchsine must first undergo transformation into the ammonium base, termed “rosaniline base” by Hantzsch.

According to Hantzsch and Osswald, the other colour bases of the di- and triamidotriphenylmethane dye-stuffs behave in a similar manner. In addition to the known colourless carbinol bases we have here also coloured am-

monium bases, all of which contain the atomic complex,



wherein R may either represent hydrogen or a monovalent group, *e.g.*, CH₃.

Whereas the existence of such coloured ammonium bases seems definitely settled, divergent opinions prevail on the nature of the aforesaid coloured rosaniline base soluble in ether. There are two hypotheses.

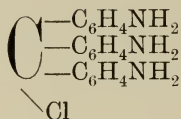
According to Hantzsch the rosaniline ammonium base exists solely in the state of an aqueous solution; and he asserts that ammonium bases cannot exist in the solid state, nor are they soluble in ether.

Hence the aforesaid coloured rosaniline base must be something different—perhaps an imide base formed by the elimination of water from the rosaniline ammonium base. In support of this view he cites the circumstance that rosanilines with substituted amido groups, *e.g.*, Crystal Violet and Malachite Green, wherein such elimination of water is impossible, do not furnish coloured bases soluble in ether.

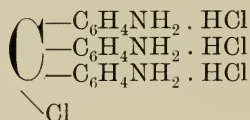
The author, on the other hand, is of opinion that his coloured rosaniline base should be regarded as rosaniline ammonium base. According to his researches the behaviour of Crystal Violet and Malachite Green speaks against and not in favour of the assumption of an imide base, since in the above-described reaction these dyes behave quite analogous to fuchsine, if not exactly the same.

An entirely different conception of rosaniline and the mechanism of saline combination therewith is formulated by Rosenstiehl, according to whom rosaniline is a tertiary

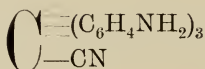
alcohol, and its chloride the chlorine ester thereof, in agreement with the formula * :—



This view is based solely on the circumstance that he succeeded in introducing four atoms of chlorine into rosaniline, and obtained a product with the formula :—



This conception, however, is opposed by the properties of the rosaniline-cyanide prepared by E. Fischer and W. L. Jennings,† which properties are quite the converse of those exhibited by rosaniline. Rosaniline-cyanide has been definitely recognised as a derivative of triphenylacetoneitril, $\text{C} \equiv (\text{C}_6\text{H}_5)_3$, and has the composition :—



Rosaniline-cyanide.

Now, since similarly constituted chlorine and cyanogen compounds exhibit great similarities, it follows that, if rosaniline chloride really has the formula ascribed to it by Rosenstiehl, it must be very similar to Fischer and Jennings' rosaniline-cyanide. This, however, is by no means the case. Rosaniline chloride is highly coloured, readily soluble in water, and easily decomposed by alkalis; whilst rosaniline-cyanide, on the contrary, is colourless, insoluble in

* *Bull. Soc. Mulhouse*, 1893, **63**, p. 195.

† *Berl. Ber.*, 1893, **26**, 2221.

water, and stable towards alkalis; in fact, behaves in a manner quite analogous to leucaniline, and in accordance with the formula given above.

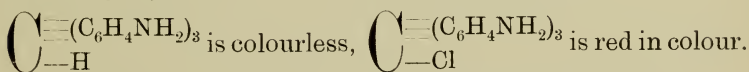
The untenability of the Rosenstiehl hypothesis is further revealed by the existence of a coloured rosaniline base, as well as by the fact—confirmed both by Miolati and subsequently by Hantzsch—that fuchsine behaves like a salt, just the same as other dye-stuffs, to be described later on, such as Methylene Blue and Phenosafranine, which cannot be assumed to have formulæ coinciding with Rosenstiehl's hypothesis. Miolati also found that leucaniline furnishes a compound with 4 molecules of hydrochloric acid.

In connection with this question stands also the opinion expressed by V. von Richter* that the coloration of the coloured triphenylmethane derivatives is influenced by the circumstance that, in this case, the radicle directly combined with the methane carbon is possessed of opposite chemical functions to those of the radicles occupying the para position towards the methane carbon in the phenyl groups. Conversely, when the radicles in question have similar chemical functions, the corresponding compounds will be colourless, *e.g.* :—



Trinitrotriphenylmethane.

Sodium compound of same.



Leucaniline.

Rosaniline chloride (Richter and Rosenstiehl).

This assumption of Richter's has recently been elevated by Rosenstiehl† to the dignity of a general rule applying to the whole of the triphenylmethane derivatives.

* *Berl. Ber.*, 1893, **21**, p. 2477; *Soc. Chim.*, Paris, **33**, pp. 342 and 426.

† *Bull. Soc. Mulhouse*, 1894, pp. 181-200.

In one particular the views of all the above-named authors agree, *viz.*, that elimination of water accompanies the formation of the rosaniline salt. That this is so is confirmed by the behaviour of a simple, but similarly constituted amidoalcohol. O. Fischer prepared p. amidobenzyl alcohol $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, and studied its behaviour during the formation of the saline compound. Under these conditions it was found that this substance first combines with hydrochloric acid to form a salt of normal composition, $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$, which becomes yellow when dried, and then acquires the faculty of dyeing silk yellow in an alcoholic solution. On dissolving this yellow salt in water, the solution rapidly becomes colourless, and the normal colourless salt is again deposited.

In the case of diamidotriphenylcarbinol, $\text{C} \begin{array}{l} \text{---} \text{C}_6\text{H}_5 \\ \text{---} \text{C}_6\text{H}_4\text{NH}_2 \\ \text{---} \text{C}_6\text{H}_4\text{NH}_2 \\ \text{---} \text{OH} \end{array}$,

the base of the Malachite Green series, the formation of the coloured salt goes on in the same way, but much more slowly than with rosaniline.

p. Monamidotriphenylcarbinol, $\text{C} \begin{array}{l} \text{---} (\text{C}_6\text{H}_5)_2 \\ \text{---} \text{C}_6\text{H}_4\text{NH}_2 \\ \text{---} \text{OH} \end{array}$ (4), furnishes

only a hydrochloride of normal composition, $\text{C} \begin{array}{l} \text{---} (\text{C}_6\text{H}_5)_2 \\ \text{---} \text{C}_6\text{H}_4\text{NH}_2 \\ \text{---} \text{OH} \end{array} \cdot \text{HCl}$,

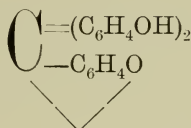
tion, and cannot be converted into a tinctorial anhydro salt by elimination of water. The incapacity of this substance to furnish dye-stuffs must be attributed to its very faint basic properties; it will only dye tannined cotton.

Consequently, the above-mentioned p. amidobenzyl alcohol, $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, may be regarded as the simplest type of tinctorial carbinol base.

Analogous conditions prevail in the group of rosolic acid dye-stuffs. In this case, trioxytriphenylmethane,

$\text{C} \begin{array}{l} \equiv (\text{C}_6\text{H}_4\text{OH})_3 \\ -\text{H} \end{array}$, corresponds to the leuco base of rosaniline,

whilst the place of the rosaniline base is filled by aurine, an anhydride of trioxytriphenylcarbinol, corresponding to the formula :—

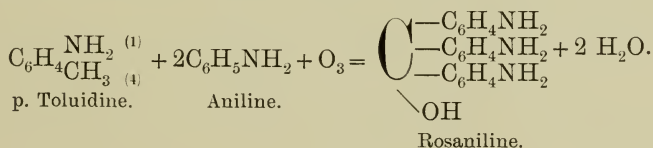


Carbinol itself, $\text{C} \begin{array}{l} \equiv (\text{C}_6\text{H}_4\text{OH})_3 \\ -\text{OH} \end{array}$, is unknown, though

triacetylaurine is a derivative therefrom. Aurine is but slightly coloured, its tinctorial character only appearing in the saline compounds.

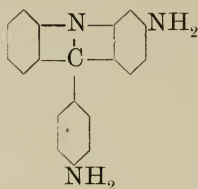
METHODS OF PREPARING THE TRIPHENYLMETHANE DYE-STUFFS.

(a) By the oxidation of para amines together with such bases as are capable of furnishing rosaniline :—



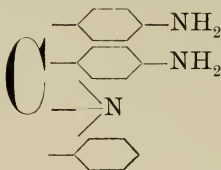
This method is employed for the production of Fuch-sine; arsenic acid or nitrobenzol is used as the oxidising agent.

The process explained on an earlier page (142) also follows a somewhat different course, whereby an acridine dye-stuff, Chrysaniline, is formed. This has the formula :—

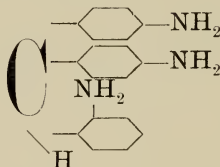


Diamidophenylacridine or Chrysaniline.

or, if written as a triphenylmethane derivative :—



This dye-stuff, which is always formed along with Fuchsine, therefore owes its occurrence to a partial ortho condensation, wherein the compound



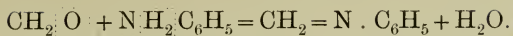
must be imagined as an intermediate product.

In this process, as is well known, the methane carbon is obtained from the methyl group of the p. toluidine employed.

According to patents by L. Cassella & Co., the course of the reaction is improved in a quantitative sense when the methane carbon is supplied by simple compounds of the fatty series, such as methylsulphuric acid or methyl alcohol, which substances should be added to the fuchsine melt.

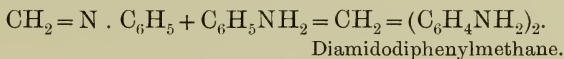
(b) The condensation of formaldehyde with aniline furnishes anhydroformaldehydeaniline* :

* If aniline be replaced in this process by rosaniline, safranine, etc., there results, according to Trillat, a new class of dye-stuffs: *Compt. rend.*, **116**, 1382-1385; (*Berl. Ber.*, 1893, p. 688).



Formaldehyde. Aniline. Anhydroformaldehyde-
aniline.

On heating this product with aniline and aniline chloride, it is converted, by atomic displacement, into diamidodiphenylmethane :

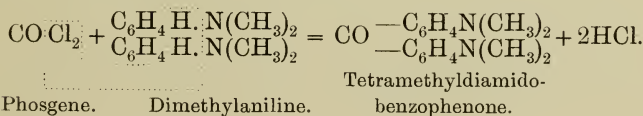


This latter is easily convertible into triphenylmethane dye-stuffs, and yields Fuchsine direct when heated with aniline chloride, in presence of an oxidising agent. This method, which has been patented by the Hoechst Farbwerke, is termed the new fuchsine process, and forms the most important novelty in this branch.

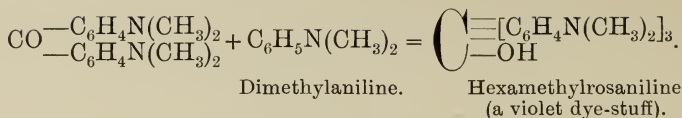
The progress hereby attained is, according to Friedlander, based upon the largely increased yield of dye-stuff, diminished troublesome residue, and the possibility of obtaining uniform compounds, instead of a mixture of homologues as hitherto. The reaction is also capable of manifold application.

Fuchsine, New Fuchsine, and different Acid Violets are produced by this method, though the greater part of the Fuchsine consumed is still prepared by the nitrobenzol process.

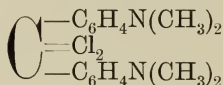
(c) When phosgene gas, COCl_2 , is allowed to react on dimethylaniline in the presence of zinc chloride, tetramethyldiamidobenzophenone is formed :—



This latter can then be readily condensed, by the aid of various bases, into a triphenylmethane derivative, *e.g.* :—

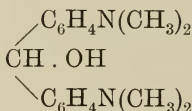


In such condensations preference is given to the chloride of the said benzophenone derivative :—



Dye-stuffs prepared by this method are also known by the name of phosgene dye-stuffs.

(d) By condensing tetraalkylated diamidobenzhydrol, *e.g.* :—

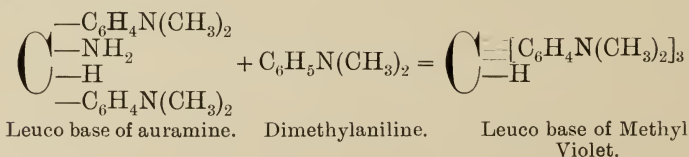


(obtained from the corresponding methane derivative by oxidation) with bases, phenols, and acids, a number of triphenylmethane dye-stuffs (Chrome Violet, Chrome Blue, and a series of Acid Violets) are obtained.

As Fr. Bayer & Co. have recently found, the above hydrol can—contrary to expectation—be condensed with naphthalene, naphthalene sulpho acids, nitrobenzol, etc., and even with finished dye-stuffs (Oxazines).

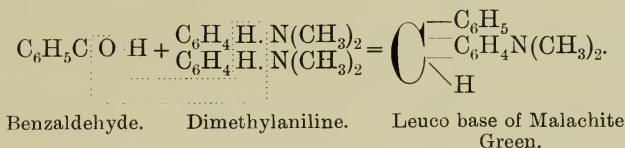
The constitution of the resulting leuco compounds, which have to be oxidised to convert them into dye-stuffs, depends entirely on the conditions under which the operation of condensation was carried on.

(e) In a similar manner, dye-stuffs of the rosaniline group, *e.g.* :—



may be obtained by condensing leucauramines with tertiary bases.

(f) Benzaldehyde may be condensed by bases, in presence of acids or zinc chloride, to dye-stuffs of the diamido-triphenylmethane—or Malachite Green series:—



If benzaldehyde be replaced by its p. nitro or p. amido derivative, rosaniline dye-stuffs are obtained.

(g) By the condensation of benzotrichloride, $\text{C}_6\text{H}_5\text{CCl}_3$, with bases or phenols. Formerly a number of dye-stuffs of the Malachite Green and rosolic acid series were prepared by this means, but the method has now been abandoned.

A few special methods will be described in their proper places later on.

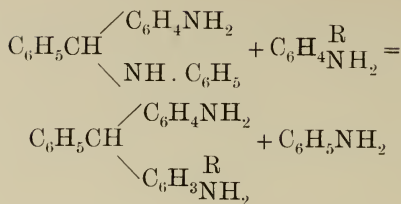
Triphenylmethane dye-stuffs are also formed:—

(a) According to K. Heumann, carbon tetrachloride, CCl_4 , can be condensed to rosaniline and rosolic acid dye-stuffs, by bases and phenols in presence of aluminium chloride. The process, however, does not run smoothly, and is, therefore, not used in practice.

(b) From p. amidobenzyl alcohol $(\text{C}_6\text{H}_4\text{CH}_2\text{OH})_{\text{NH}_2}$ and aniline (Kalle & Co.).

(c) From methylenediphenylhydroxylamine, $\text{C}_6\text{H}_5\text{N} - \text{CH}_2 - \text{N} \cdot \text{C}_6\text{H}_5$, produced from formaldehyde and phenylhydroxylamine, and aniline (Kalle & Co.).

(d) By displacing benzylidene compounds with amines, *e.g.*:—



(M. L. Br.).

(e) By condensing nitrobenzal chloride, $\text{C}_6\text{H}_4 \begin{array}{l} \nearrow \text{CHCl}_2^{(1)} \\ \searrow \text{NO}_2^{(4)} \end{array}$,

or nitrobenzyl chloride, $\text{C}_6\text{H}_4 \begin{array}{l} \nearrow \text{CH}_2\text{Cl}^{(1)} \\ \searrow \text{NO}_2^{(4)} \end{array}$, with aromatic bases.

(f) By the action of certain methane derivatives, such as iodoform, picric chloride, etc., on aniline:

(g) Rosaniline dye-stuffs can be obtained by heating rosolic acid along with ammonia or aniline.

(h) From triphenylmethane, by nitration, and reducing the resulting trinitrophenylmethane.

Finally, a number of dye-stuffs of this group are also obtained from Fuchsine (see below).

General properties and behaviour of the Diamido- and Triamido-triphenylmethane Dye-stuffs.—

Nearly all these dye-stuffs are met with in commerce as chlorides; more rarely as acetates, oxalates, or double salts of zinc chloride. With the exception of the greens, they all exhibit in a decided degree the peculiarity that, when in thick layers in the solid state, they assume colours complementary to their own. Thus, for instance, Fuchsine, which is red when in a finely divided state or in solution, is green in the solid, commercial form.

The best method of dissolving these dye-stuffs is in distilled water acidified with acetic acid, since if dissolved in pure water they undergo a still unexplained alteration. This behaviour is probably due to partial hydrolytic dis-

sociation, though this has only been proved in the case of Fuchsine.*

The solutions are decolorised by an excess of alkali or acid, and by reducing agents, the products being either the carbinol bases, poly-acid salts, or the leuco bases, according to the reagents employed.

As dye-stuffs, they belong to the "substantive," "monogenetic," "dye" class in the sense used by Perger. In the dyeing process the colour bases alone are absorbed, so that it is immaterial which salt is used. They dye silk and wool direct, without any adjunct; cotton after treatment with tannin.

The dyeings are very handsome, but for the most part fugitive to light. Their chief application is in cotton dyeing and calico printing. In practice they are grouped along with the basic or tannin dye-stuffs. Their sulpho acids are acid dye-stuffs which play an important part in the dyeing of wool and silk.

Fuchsine.—Commercial Fuchsine is a mixture of the chlorides (more rarely the acetates) of para- and homo-rosaniline. It is prepared by oxidising "Aniline oil for red"—*i.e.*, a mixture of aniline, ortho- and para-toluidine—with arsenic acid or nitrobenzol. In the first-named method, the mixed bases in question are heated to 170-180° C., along with a syrupy (about 70 per cent.) solution of arsenic acid for 8-10 hours. The product of this reaction, the so-called "fuchsine melt," is comminuted and lixiviated, the arsenic being partly neutralised with lime, and the Fuchsine finally "salted out" (or separated by means of common salt), to be afterwards purified by re-crystallisation in water.

The fuchsine melt contains, in addition to Fuchsine, a number of other dye-stuffs, such as Violaniline, Mauveine,

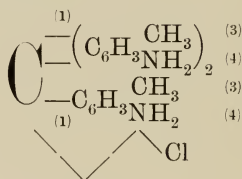
* Georgievics, *Mitth. k. k. Techn. Gew.-Mus.* Wien, 1894, p. 214.

Chrysaniline, etc., which are also in part isolated (Phosphine).

In the nitrobenzol process (Coupier, 1886) aniline and a little aniline chloride are mixed with crude nitrobenzol and iron filings, and heated to 190° C. for 10-24 hours, the remainder of the treatment being the same as in the other process. In this case the nitrobenzol acts as oxidising agent, the iron salts serving as carriers of oxygen.

At present, the nitrobenzol process is almost exclusively used in preparing Fuchsine,* the other method having been abandoned on account of the poisonous nature of the arsenic. For many purposes, however, especially the production of large crystals for export, importance still attaches to the Fuchsine obtained by the arsenic acid process.

Both Fuchsine and New Fuchsine are prepared by the Hoechst Farbwerke according to the new process. New Fuchsine is a tritolyrosaniline,



and is produced from orthotoluidine. It possesses the advantage of being more soluble in water than ordinary Fuchsine, but is unsuitable for the manufacture of Aniline Blue.

The purest commercial form of Fuchsine is Diamond Fuchsine; whilst more or less impure grades are sold as Rubine, Magenta, Cerise, Amethyst, Garnet, Chestnut, etc.

The yellower the tinge of Fuchsine the greater its value, on which account it is frequently mixed with some yellow

* The formation of Fuchsine from p. nitrodiamidotriphenylmethane is of theoretical interest. This compound, when slightly reduced, gives a phenylhydroxylamine, which, on being heated with HCl, is converted into Fuchsine (Prudhomme, *Compt. rend.*, **121**, p. 891).

dye-stuff, and sold as Fuchsine extra Yellow, Fuchsine Scarlet (mixed with Auramine), Cardinal, Russian Red (mixed with Safranine), Juchten Red (Grenadine or Cerise, shaded with Chrysoidine), etc.

The practical importance of Fuchsine consists less in its properties as a dye-stuff, than in the circumstance that it serves as a raw material for the production of a whole series of other rosaniline dye-stuffs.

PRODUCTION OF VIOLET, GREEN AND BLUE DYE-STUFFS FROM FUCHSINE.

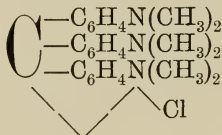
If the hydrogen of the amido groups in Fuchsine be replaced by methyl or ethyl groups, violet dye-stuffs are formed, the colour of which approximates more closely to blue in proportion as a larger number of alkyl groups have entered into the Fuchsine molecule. On treating these violet substitution products with methylchloride, ethyliodide, etc., we obtain additive products forming green dye-stuffs. Finally, the substitution of the hydrogen of the amido groups in Fuchsine by phenyl groups, furnishes violet to blue dye-stuffs. Only one hydrogen atom of each amido group can be replaced by phenyl.

Of late a number of new dye-stuffs have been prepared from Fuchsine in other ways. Thus, for example, nitration furnishes dye-stuffs, which produce a garnet red (B. A. S. F.) on wool, silk and tannined cotton. Finally, the diazotisation of Fuchsine, followed by combination with salicylic acid and o. creosotic acid ($\text{C}_6\text{H}_3 \cdot \overset{1}{\text{CH}_3} \cdot \overset{2}{\text{OH}} \cdot \overset{3}{\text{COOH}}$), furnishes triazo dye-stuffs, which, when applied to chromed wool, give yellow shades fast to light and milling (Soc. Anon. St. Denis). These products, however, are not met with in commerce.

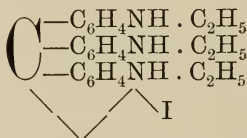
By treating leucaniline with fuming sulphuric acid followed by oxidation, there is formed a blue basic dye-stuff of

particular beauty (M. L. Br.); its constitution is unknown and it is not yet put on the market.

Methyl Violet (Violet de Paris).—Under this name figure a whole series of commercial dye-stuffs, which are mostly mixtures of methylated rosanilines. Those with a red tinge contain few methyl groups and are designated Methyl Violet, R, 2R, 3R, etc.; the more they diverge from the parent substance (rosaniline) by the absorption of a larger number of methyl groups, the more does their colour incline towards blue. These marks are indicated by the letters B, 2B, 3B, etc. From the foregoing it results that the bluest grade of Methyl Violet must be a hexamethylrosaniline,



These dye-stuffs were formerly prepared by methylating or ethylating rosaniline (by the action of halogen alkyls), and the first violet of the group was obtained by A. W. Hoffman in this manner. This "Hoffman's Violet" is the iodide of triethylrosaniline, corresponding to the formula:—



It is now merely of historical interest.

At present only the red marks of Methyl Violet are prepared by methylating rosaniline. The most usual method now employed consists in oxidising dimethylaniline with cupric chloride in presence of phenol. The course of this interesting reaction is as follows: A CH_3 group of dimethylaniline is oxidised to formaldehyde, which condenses with the resulting methylaniline and the unaltered dimethylaniline to

a mixture of penta- and hexa-methylrosaniline. Consequently, diethylrosaniline, which does not contain any CH_3 group, does not furnish a violet when treated in the above manner; but if heated with formaldehyde the formation of violet occurs in abundance. In this process of manufacturing violet from dimethylaniline, the part played by the added phenol has not yet been elucidated.*

The violet prepared in the manner described can be converted into the bluest grade of Methyl Violet (6B), by heating with benzyl chloride; more recently a similar product has been prepared direct from phosgene and dimethylaniline, and is termed Crystal Violet (hexamethylrosaniline).

The following violet dye-stuffs are nearly allied to Methyl Violet in composition and behaviour:—

Ethyl Violet contains ethyl groups in the place of methyl groups; *Benzyl Violet* is a more or less benzylated Methyl Violet; *Regina Violet* is the name given to tolyl- and diphenylrosaniline. Finally, Methyl Violet is also frequently mixed with other dye-stuffs: *Dahlia*, *Primula*, etc., are mixtures of Methyl Violet with Fuchsine; *Indigo Blue*, *Benzyl Blue*, and *Peacock Blue* are names applied to mixtures of Methyl Violet and Malachite Green, etc.

Like Fuchsine, the chief use of Methyl Violet is in cotton dyeing. In medicine it is employed as an antiseptic, under the name "Blue Pyoctanine" (see Introduction).

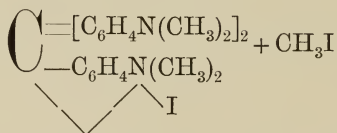
Latterly, a number of new dye-stuffs, imparting a violet blue colour to wool, silk, and tannined cotton, have been prepared from Methyl Violet by nitration (Soc. Anon. Mat. Col. St. Denis).

* Wedekind has recently recorded the production of Methyl Violet from dimethylaniline and p. nitrobenzylchloride, wherein the nitro group is the oxidising agent (*Ann. Ch.*, **307**, p. 283).

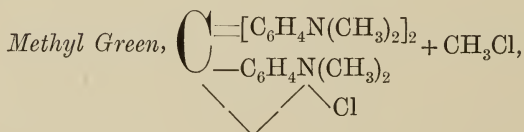
THE GREEN ROSANILINE DYE-STUFFS.

Aldehyde Green.—This, the first artificial green dye-stuff, owed its discovery to the advice given by a photographer to a dyer, with the object of improving the fastness of Aldehyde Blue, namely, to fix the colour with sodium hyposulphite in the same manner as a photographic negative. The blue (or violet) in question was obtained by Lauth through acting with sulphuric acid on a mixture of rosaniline and aldehyde; and is changed to green when treated with sodium hyposulphite. This green was largely used for dyeing silk and wool. It probably contains sulphur. According to recent researches, with a view to elucidating its constitution, it is derived from quinoline.* It was soon displaced by

Iodine Green, which is a dye first discovered in the mother liquor from Iodine Violet, and found to be an addition product of this latter and methyl (or ethyl) iodide. It is prepared by treating Methyl Violet with Methyl Iodide; and if we here start with hexamethylated violet, the composition agrees with the formula:—



At one time it was largely used. If, in the above process, methyl iodide be replaced by methyl chloride, the product will be



* "Aldehyde Green" (Origin), Gattermann and G. Wichmann, *Berl. Ber.*, 1889, 234 a; "Aldehyde Blue," *ibid.*, 1889, 227 a; "Constitution of Aldehyde Green," Miller and J. Plöchl, *ibid.*, 1891, 1700 a.

a dye-stuff formerly of great importance as the successor of Iodine Green, though now its use has declined. Like Iodine Green, it has the disadvantage of parting with methyl chloride when heated to 110-120° C., and thereby becoming converted into Methyl Violet. It is chiefly used in cotton dyeing and calico printing, being faster to light than Malachite Green (see later), but is not well adapted for dyeing wool. In commerce it is usually met with as a double salt of zinc chloride.

THE BLUE ROSANILINE DYE-STUFFS.

A number of commercial dye-stuffs—Rosaniline Blue, Aniline Blue, Spirit Blue, Lyons Blue, Parma, etc.—consist of variable mixtures of mono-, di- and triphenylrosaniline in the form of chlorides. The nearer they are to consisting

entirely of triphenylrosaniline, $\text{C} \begin{array}{l} \text{---C}_6\text{H}_4\text{NH} \cdot \text{C}_6\text{H}_5 \\ \text{---C}_6\text{H}_4\text{NH} \cdot \text{C}_6\text{H}_5 \\ \text{---C}_6\text{H}_4\text{NH} \cdot \text{C}_6\text{H}_5 \end{array}$, the greater

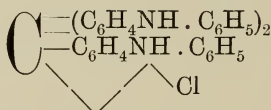
their tendency to a pure blue shade, and the less reddish their appearance (as already mentioned, not more than three phenyl groups can be introduced into the molecule of Rosaniline). The purest Rosaniline Blues are distinguished by retaining their pure blue colour under gas light.

The conversion of Rosaniline into blue by phenylation was discovered by Girard and De Laire in 1861, the first product—which was insufficiently phenylated and consequently of a very reddish tinge—being sold as Bleu de Lyon (Lyons Blue). The present Spirit Blue, or Rosaniline Blue, is prepared by heating together, for about four hours, a mixture of rosaniline and nearly chemically pure aniline (the so-called “Aniline oil for Blue”), with a little benzoic acid. The product is partially neutralised with hydrochloric acid, and the chloride of the colour base is crystallised out.

To ensure completeness of phenylation an excess of aniline must be taken and the latter must also be pure (*i.e.*, free from toluidine), since toluidine produces reddish-tinged blues. The benzoic acid is recovered unaltered from the melt, but the part* it plays in the process is unexplained.

The discovery of Rosaniline Blue was of epoch-making importance to the dye-stuff industry, though at the present time its practical application is very restricted.

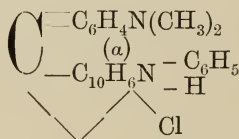
Diphenylamine Blue.—This dye-stuff, discovered by Girard and De Laire in 1866, successfully competed with the first Rosaniline Blue. It is formed by heating diphenylamine, $\text{C}_6\text{H}_5\text{NH} \cdot \text{C}_6\text{H}_5$, with oxalic acid, and consists of triphenyl-rosoaniline : †



but is not identical with Rosaniline Blue.

A large number of green to blue dye-stuffs have been prepared from tetramethyldiamidobenzophenone and tetramethyldiamidobenzhydrol. As already mentioned, the latter is distinguished by its great susceptibility to condensation, and has of late been largely used for the production of basic, acid and mordant dye-stuffs.

Victoria Blue.—The various products put on the market under this designation are phosgene dyes. The mark B is prepared by condensing tetramethyldiamidobenzophenone chloride with phenyl α -naphthylamine, and, therefore, corresponds to the formula :—



* First observed by Wanklyn (1862).

† It is produced from diphenylamine and p. nitrobenzylchloride. Wedekind, *Ann. Ch.*, **307**, p. 233.

If the latter component be replaced by methylphenyl α -naphthylamine, we obtain Victoria Blue 4R (B.); whilst the mark R (B.) is produced with mono-ethyl α -naphthylamine, and is identical with New Victoria Blue B (By.).

Victoria Blue plays an important part in wool dyeing, the colours being handsome and fast to milling, though, unfortunately, fugitive to light.

Night Blue.—This very handsome but fugitive blue is—like Victoria Blue—prepared from tetraethyldiamidobenzophenone and p. tolyl α -naphthylamine. It owes its name to the beauty of its colour under artificial illumination.* One of its noteworthy properties is that of furnishing insoluble compounds with many dye-stuffs, *e.g.*, picric acid, Naphthol Yellow S, on which account it can be used for the quantitative estimation of these substances.*

Night Blue is used, to a small extent, for dyeing silk.

A new and technically important dye-stuff of this group is Fr. Bayer's

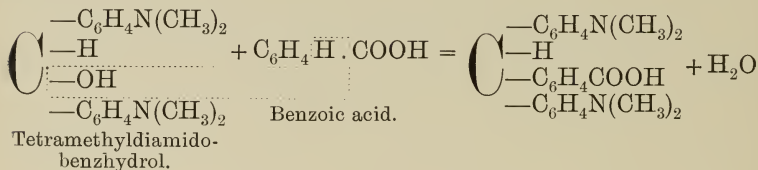
Turquoise Blue, which is prepared by the condensation of tetramethyldiamidobenzhydrol and p. nitrotoluol. On account of its particularly clear shade and great fastness towards alkalis, it is largely used in calico printing and the manufacture of lakes. Similar dye-stuffs are *New Solid Green* (*Ges. Chem. Ind. Basel*), from dichlorbenzaldehyde and dimethylamine and the *Firn Blue* (Glacier Blue) of the same makers—from m. nitro-o.-chlorbenzaldehyde and monoethyl-o.-toluidine—both very handsome but expensive materials.

Fr. Bayer & Co. produce pure blue dye-stuffs, containing an acetylated amido group in the ortho position towards the methane carbon, by the aid of tetramethyldiamidobenzhydrol and m. phenylenediamine; the latter is used either in a

* These insoluble compounds are probably salts analogous to the compounds of Fuchsine with acid dye-stuffs, as prepared by Seyewetz: *Chem. Ztg.*, 1888, p. 52; *Zeits. Angew. Chem.*, 1888, Dec.

ready-acetylated condition, or else acetylated after condensation.

To this class also belong the Chrome Dyes of Fr. Bayer & Co. As an example of the production and composition of these may be cited *Chrome Green*, prepared by condensing tetramethyldiamidobenzhydrol with benzoic acid in presence of sulphuric acid :—



the resulting condensation product furnishing, on oxidation, a dye-stuff, the salt of which yields a green lake with chrome.

If, in this process, the benzoic acid be replaced by salicylic acid, the product is Chrome Violet; if by α -oxynaphthoic acid, Bayer's Chrome Blue is obtained. As in the case of the green, these dye-stuffs have received their names from the colour of their chrome lakes. The latter are very bright and fast to milling, but fugitive to light. These dye-stuffs are used in calico printing.

SULPHONIC ACIDS OF THE ROSANILINE DYE-STUFFS.

In 1862 it was discovered by Nicholson that insoluble Rosaniline Blue, when heated with concentrated sulphuric acid, underwent conversion into a blue dye-stuff soluble in water. This discovery was of far-reaching, practical importance, it being afterwards found that many other dye-stuffs could be advantageously modified by the same treatment. True, the introduction of sulpho groups weakens the tinctorial power of the dye-stuffs in general; but, on the other hand, the resulting sulpho acids, or their alkali salts (which alone are

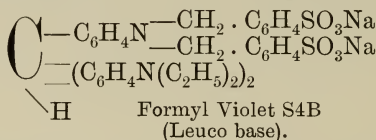
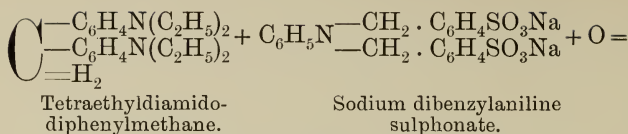
used in practice), are all soluble in water, and can be used in the same way as acid dye-stuffs, a circumstance rendering them especially valuable for dyeing wool. Again, whilst Methyl Violet, for example, is itself soluble in water, it is far less suitable for dyeing wool than is the Acid Violet it furnishes on sulphonation, owing to its tendency to come off.

This Nicholson method of converting basic dye-stuffs into soluble acid dye-stuffs is of great practical importance, and is applied to all classes of dyes. The sulpho groups can be introduced either by sulphonating the finished dye-stuffs, or their leuco compounds, or finally by employing previously sulphonated components in their preparation.

Fuchsine S (Acid Fuchsine).—The commercial products sold under this title are acid sodium salts of fuchsine di- or trisulphonic acids. It is prepared by treating Fuchsine with fuming sulphuric acid.

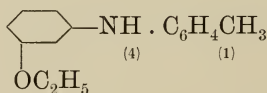
Acid Violet.—This is the general name applied to a series of dye-stuffs, which were very important at one time, but have declined since the introduction of the equalising azo dye-stuffs (Azo Fuchsine, Chromotrope, etc.). They are sodium salts of sulphonated Methyl Violet dye-stuffs, and are prepared for the most part by benzhydrol condensation. Whilst the red marks may also be azo dye-stuffs, the blue marks are merely derivatives of triphenylmethane. A number of them are not uniform products, but are the result of mixing red and blue grades, Acid Violet 4RS (By.), for instance, being a mixture of an Acid Violet with Fuchsine S; whilst Wool Blue S (B.) is a mixture of Acid Violet with 7B and Blue Green S, etc.

Formyl Violet (5BN, S4B, etc.) is made by Cassella, and is distinguished for its relatively good fastness to milling. It is similar to Bayer's Acid Violet 5B. Its formation can be explained by the following equation:—

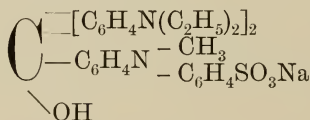


The corresponding dye-stuffs of tetramethyldiamidobenzhydrol are the cheap Acid Violet 4B extra (By.) and the New Guinea Violet 4B (Act.). Fast Acid Violet 10B (By.) is prepared from the hydrol of dimethylaniline and a new methylbenzylanilinedisulphonic acid, in which one of the sulpho groups is found in the benzyl group, the other in the benzol nucleus (in meta position to the amido group).

Acid Violet 6BN (B.), notwithstanding its low resistance to alkalis, is a largely used dye-stuff, prepared from tetramethyldiamidobenzophenone and m. ethoxyphenyl-p.-tolylamine, this component being produced from resorcin and p. toluidine :



Alkali Violet.—This dye-stuff, first prepared by the Badische Anilin- und Sodafabrik, is the sodium salt of a monosulphonic acid of tetraethylmethylphenylrosaniline, corresponding with the formula :—



It possesses the remarkable property of dyeing wool in an alkaline, acid, or neutral bath, the dyeings being distinguished by particular fastness to milling. For these reasons, Alkali Violet is a valuable dye-stuff. It is also used

for blueing white silk, and is similar to Bayer's Alkali Violet R.

Alkali Blue is the sodium salt of the monosulphonic acid of Rosaniline Blue. It is largely used for wool and silk, on which it produces a very handsome pure blue, fast to milling. The manner in which this dye-stuff is applied is peculiar, and differs entirely from usual dyeing methods. The goods are first heated in an alkaline solution of Alkali Blue, the dye-stuff being thereupon absorbed in the form of a colourless compound; on then treating the fibre with an acid, the blue coloration is developed immediately.

Navy Blue, **Water Blue**, **Blackley Blue**, **Cotton Blue**, **Methyl Blue**, **Silk Blue**, **China Blue**, **Bavarian Blue**, **Sedan Blue**, etc. Under these names a number of more or less pure blue dye-stuffs are put on the market, most of them being ammonium (or sodium) salts of the di- and trisulpho acids of Rosaniline Blue. Frequently one and the same dye-stuff is sold under different names, **Cotton Blue** and **Water Blue**, for instance, being identical.

The two first on the list are reddish in shade, the remainder more of a blue cast.

Nicholson Blue is the commercial name of a mixture of Alkali Blue and Water Blue in nearly equal parts.

These dye-stuffs are used for a variety of purposes; Water Blue, for example, being largely employed for dyeing cotton, silk, mixed fabrics, and in paper making.

Fast Acid Blue B (Bayer) is a new "Night Blue" obtained from the hydrol of dimethylaniline and α -naphthylaminedisulphonic acid. It is not very fast to light, but equalises well, and is fast to alkalis. Chemically identical with this is Intensive Blue (By.)

It is worthy of note that several of these dye-stuffs, *e.g.*, Water Blue, can be used for dyeing tanned cotton.

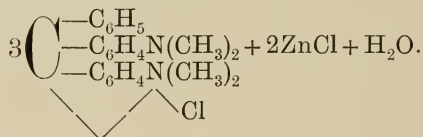
Despite, therefore, their conversion into a decidedly acid character through the introduction of sulpho groups, these dye-stuffs still retain their original basic properties to such an extent as to be capable of dyeing cotton in the same manner as the basic dye-stuffs.

DIAMIDOTRIPHENYLMETHANE DYE-STUFFS, OR DYE-STUFFS OF THE MALACHITE GREEN SERIES.

All the older dye-stuffs of this class are green in colour, and it is only of late that blue dye-stuffs of the series—the various Patent Blues—have been obtained.

The green members of the group are formed from diamidotriphenylmethane by replacing the amido hydrogen with methyl, ethyl, benzyl, etc., groups, the benzylated dye-stuffs in particular furnishing pure shades. They are all basic, and can be converted into acid dye-stuffs by sulphonation. The basic dyes are used for cotton and in the manufacture of lakes, whilst the acid dyes are employed for wool and silk.

Malachite Green, Benzaldehyde Green, Victoria Green, Solid Green, Benzoyl Green, New Green, Vert Diamant (Diamond Green). This, the first member of the group, was discovered by O. Fischer in 1877. It is mostly put on the market as a double salt of zinc, occasionally also as an oxalate, and is a tetramethyldiamidotriphenylmethane :



Malachite Green has, to a large extent, displaced the older Methyl Green, which it surpasses in tinctorial power. It is prepared in the following manner (Fischer's method) :

Benzaldehyde (oil of bitter almonds) is condensed, by 2 molecules of dimethylaniline in presence of hydrochloric or sulphuric acid, to the leuco base of tetramethyldiamido-triphenylmethane, which in turn is converted, by oxidation with lead peroxide and hydrochloric acid, into the colour base, which is finally salted out with zinc chloride and common salt. At one time it was also prepared by Doebner's method : condensation of benzotrichloride and dimethylaniline, in presence of zinc chloride.

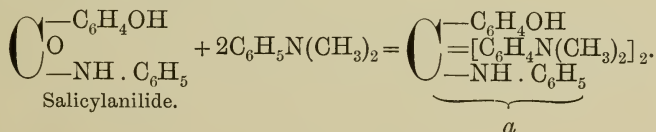
Brilliant Green, Ethyl Green, Emerald Green, New Victoria Green, Solid Green J, etc. These names are applied in commerce to the tetraethyl derivative corresponding to Malachite Green. It gives dyeings of a somewhat yellower tinge.

New Solid Green or New Victoria Green extra is entirely analogous in composition to Malachite Green, but is prepared with dichlorobenzaldehyde instead of benzaldehyde.

A Quinoline Green is prepared by condensing tetramethyldiamidobenzophenone with quinoline. It is not met with in commerce.

All these dye-stuffs give very blue-tinged green dyeings, and must, therefore, be shaded with yellow when a pure green is required.

Under certain circumstances, carbo acids, also, can be condensed to **Malachite Green** dye-stuffs with tertiary amines. Such a product is formed, according to Noetting, by the condensation of salicylanilide with dimethylaniline (in presence of phosphorus oxychloride) :



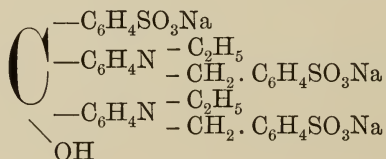
If the anilido group indicated by *a* be eliminated by the aid of hydrochloric acid, a Malachite Green dye-stuff is

obtained. This reaction is not given by the analogous derivatives of m. and p. oxybenzoic acid, or by o. nitro- and o. amidobenzoic acid. It has been observed by Fr. Bayer & Co. that a benzoic acid containing a CH_3 group in the ortho position to the carboxyl group can be condensed to greenish-blue dye-stuffs with tertiary aromatic amines.

SULPHONIC ACIDS OF THE DIAMIDOTRIPHENYLMETHANE DYE-STUFFS.

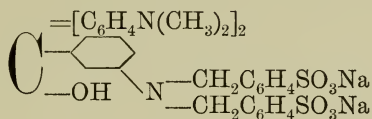
The generic name applied to the older dye-stuffs of this group is "Acid Green". They come on the market in very divergent degrees of purity, being often mixed with basic dye-stuffs, picric acid, or Naphthol Yellow, and play a highly important part in dyeing wool and silk. They are quite as fast to light as the basic green dye-stuffs whose acquaintance we have just made. The oldest member of the series, Helvetia Green, the sulpho acid of Malachite Green, is no longer on the market.

Special favour is accorded to Light Green SF yel. (B. A. S. F.), which is identical with Acid Green GG (By.), and Acid Green extra conc. (C.). It is prepared by the condensation of benzaldehyde with benzyldiethylaniline and the introduction of three sulpho groups, and, therefore, corresponds to the formula:—



It is largely employed in dyeing animal fibres and in the manufacture of lakes. Guinea Green (Act.) is a similar product, but is prepared from ethylbenzylanilinesulphonic acid.

The first advance made in this branch was the introduction of Bayer's Fast Green, obtained by first condensing m. nitrobenzaldehyde with 2 molecules of dimethylaniline, then reducing with NO_2 to NH_2 , followed by benzylation and sulphonation :—

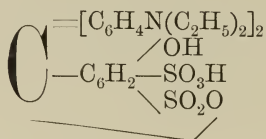


The various marks of this dye-stuff are faster to light and alkalis than Acid Green (especially the mark Fast Light Green), and compete with these, as also with Indigocarmine, a blue equalising dye-stuff of the Indigo group. A similar product is Wool Green S (B.), produced by the condensation of tetramethyldiamidobenzophenone with β -naphthol, and sulphonating the resulting product. An easier way of obtaining a handsomer product is by a patent process (Bayer), wherein the corresponding hydrol is condensed along with the G-salt of β -naphthol; it is sold under the name Wool Green BS. A similar dye-stuff is Neptune Green (B.).

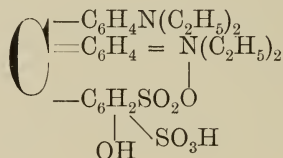
The Patent Blues may be cited as important novelties in this branch.

In 1888 it was discovered, in the colour works of Meister Lucius and Brüning, of Hoechst, that the condensation of metaoxybenzaldehyde with a dialkylated aniline, *e.g.*, dimethyl, diethyl, benzylethyl aniline, etc., furnishes leuco bases, which can be converted into very valuable greenish-blue dye-stuffs by sulphonation and subsequent oxidation. A start can also be made with meta-amido or metanitrobenzaldehyde, and then converting the amido or nitro groups into hydroxyl groups, in the usual manner, after condensation with dialkylated aniline; or a leucosulphonic acid may be fused with sodium. A typical compound of this kind is

Patent Blue V and N, which is the potassium salt of a disulphonic acid of metaoxytetraethylamidotriphenylcarbinol, corresponding to the formula :—



What is particularly remarkable in this formula, which was drawn up by Fritsch, is the assumption of a sulphone combination between a sulpho group and the carbinol hydroxyl. This is to represent the fact that Patent Blue behaves like a monobasic acid, notwithstanding that it contains two sulpho groups. Greater probability, however, attaches to the other formula, constructed by H. Erdmann, wherein the intramolecular formation of a salt between a sulpho group and an amido group is assumed.



In other points, also, Patent Blue exhibits differences in behaviour as compared with the other triphenylmethane dye-stuffs. Thus, for example, it parts quantitatively with diethylamine when boiled with alkali; but when boiled with concentrated hydrochloric acid, it gives tetraethylbenzidine, analogous to tetramethyldiamidobenzhydrol, which is oxidised to tetramethylbenzidine by lead peroxide and acetic acid.

Patent Blue A is prepared with ethylbenzylaniline (instead of diethylaniline); other marks are mixtures.

Such marks are **Patent Blue J00** (Patent Blue and Violet), Indigo substitute (Patent Blue and Victoria Violet), Patent

Navy Blue, etc. The Patent Greens O and V (M. L. Br.) are also mixtures (of Patent Blue and Acid Green).

The Patent Blues are acid dye-stuffs; they furnish very pure blue dyeings, and equalise better than indigocarmine, which they are mainly employed to replace. In fact, they have largely displaced this dye-stuff, and they play a very important part in wool dyeing. With the exception of the mark A, however, their dyeings are very fugitive to water.

Under the name **Cyanine** (B and other marks) are sold a number of dye-stuffs, prepared by oxidising Patent Blue of various kinds. Their composition is unknown, but it appears that methyl groups are eliminated, with formation of formaldehyde, during the oxidation process. In their behaviour in dyeing, they resemble Patent Blue, but give colours somewhat faster to light, and have a greater affinity for wool than the latter.

Cyanol (C.).—This handsome dye-stuff, which has largely displaced Patent Blue, is produced by condensing m. oxybenzaldehyde with 3 molecules of monoethyl-o.-toluidine, $(\text{C}_6\text{H}_4\overset{\text{CH}_3}{\underset{\text{NH}}{\text{N}}}^{(1)} \cdot \text{C}_2\text{H}_5^{(2)})$, followed by sulphonation, and finally by the oxidation of the leucodisulphonic acid to the state of dye-stuff. Indigo Blue, marks N and SGN (C.) are mixtures of Cyanol with green and red.

The **Ketone Blues** (M. R. Br.), of which the mark 4BN is the most important, are Patent Blues, prepared from benzophenones, instead of from benzaldehydes (Ger. Pat., No. 65,952).

For the most recent advance in the Patent Blue group we are indebted to a highly valuable observation made by Sandmeyer, namely, that the blue colour and fastness to alkalis of these dye-stuffs depend on the presence of a sulpho group in ortho position to the methane carbon, and not, as hitherto believed, attributable to a hydroxyl group in

the meta position to the methane carbon. The recognition of this fact constitutes the governing idea in the present-day synthetic manufacture of Patent Blue dye-stuffs.

A similar influence to that of the sulpho group is exercised by chlorine in ortho position to the methane carbon; it imparts alkali fastness to the dye, besides giving it a more bluish tinge and an acid character. According to the Clayton Co., the presence of a nitro group in ortho position to the methane carbon, also increases the fastness to alkalis. These dye-stuffs are chiefly produced by means of o. sulphobenzaldehyde ($\text{C}_6\text{H}_4\text{SO}_3\text{H}^{(2)}_{\text{COH}^{(1)}}$); though derivatives (amido-, nitro-, chloro-, etc.) of this substance are also used for the same purpose. Patents have been taken out for dye-stuffs from oxynaphthaldehydesulphonic acids, but the products do not seem to be on the market.

Another method, proposed by Fr. Bayer & Co., leading to dye-stuffs of this class with a sulpho group in the ortho position to the methane carbon, is as follows: Tetraalkyldiamidobenzhydrol is first condensed with amidosulphonic acids containing the benzhydrol in ortho position to the amido group; this is then displaced by the sulpho group,* and lastly oxidised to dye-stuff.

Finally, the introduction of a sulpho group into the ortho position to the methane carbon can also be effected by sulphonating tetraalkyldiamidodiphenylmethane, and converting the resulting monosulphonic acid into a blue dye-stuff, fast to alkali, in the usual manner (by oxidation in conjunction with amines).

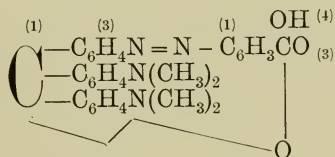
The following dye-stuffs may serve as examples :—

* This is effected by a reaction recently discovered by Gattermann. After diazotisation, the diazo group is treated with sulphurous acid and copper to ensure its displacement by the sulphonic acid group (SO_2H), which is then oxidised to a sulpho group.

Erioglaurine (Gg.) is prepared by first condensing o. sulphobenzaldehyde with 2 molecules of ethylbenzylaniline, then sulphonating (in the benzyl group), and finally oxidising. Notwithstanding its sensitivity to light, this handsome dye-stuff has largely replaced its chief competitor, Cyanol. A similar dye-stuff is the Eriocyanine of the same maker, prepared from tetramethyldiamidodiphenylmethanemonosulphonic acid and benzylated aniline (or its sulpho acid). Eriochlorine is a mixture of Erioglaurine, with a yellow dye-stuff.

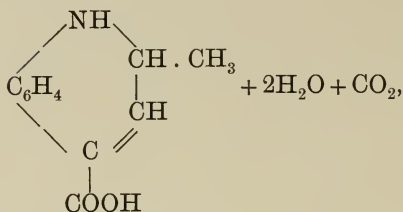
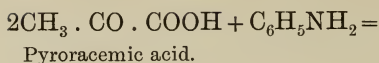
New Patent Blues B and 4B (By.) are prepared by condensing tetramethyldiamidobenzhydrol with 3. 4. or 3. 5. naphthylaminesulphonic acid, and displacing the amido group by SO_3H (see above).

Mention may also be made here of the first green azo dye-stuff, the **Azo Green** discovered by Bayer & Co. It is prepared by diazotising amidotetramethyldiamidotriphenylmethane, combining the product with salicylic acid, and oxidising the resulting leuco base. Its composition corresponds to the following formula:—

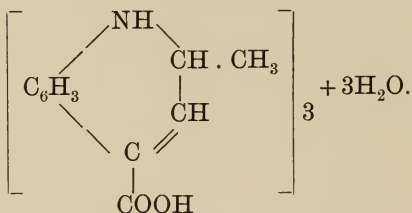
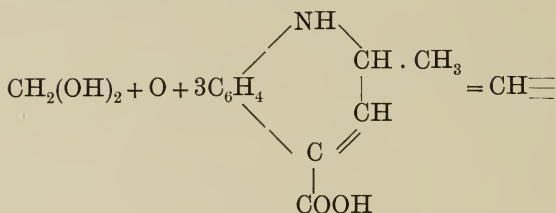


The chrome lake of this dye-stuff is used in carpet printing as a very vivid green.

The **Glauconic Acids** (O. Doebner) should also be classed with the basic triphenylmethane dye-stuffs. These are bluish-violet dyes, obtained by the successive action of pyroracemic acid and formaldehyde on aromatic primary amines, followed by the oxidation of the resulting leuco compound, *e.g.* :—

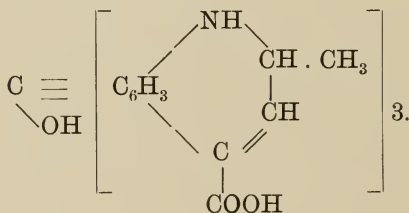


Dihydromethylchinchonic acid.



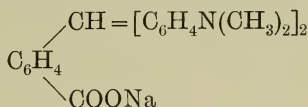
Hydroglauconic acid.

When warmed with alkalis, hydroglauconic acid is converted (by oxidation) into glauconic acid :

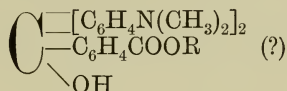


Other dye-stuffs, also belonging to the triphenylmethane derivatives, are produced from o. phthalaldehydic acid

$\text{C}_6\text{H}_4\begin{smallmatrix} \text{COH} \\ \text{COOH} \end{smallmatrix}$. This acid, used in the form of a salt, condenses with alkylated aromatic amines to phthalines, *e.g.* :—



These cannot be oxidised into dye-stuffs, but furnish bluish-green dye-stuffs when esterised :—



which are said to have the property of dyeing cotton direct (Gilliard, Monnet & Cartier, C. B., 1898, II., 1111).

ROSOLIC ACID DYE-STUFFS.

As long ago as 1834 Runge observed the production of a dye-stuff from phenol, and also found that the same was able to form very handsome colour lakes. This substance was rosolic acid, which, therefore, belongs to the oldest of the artificial dye-stuffs.

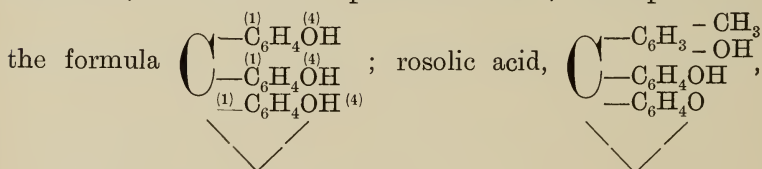
In 1861 Kolbe and Schmidt on the one hand, and Jul. Persoz on the other, simultaneously discovered a method of preparing rosolic acid by heating phenol with oxalic acid and sulphuric acid. For the elucidation of its constitution we are indebted to the same researches as established the constitution of rosaniline. As soon as the latter had been recognised as a triamido derivative of triphenylmethane, its convertibility into rosolic acid by displacing the amido groups with hydroxyl (Caro, Wanklyn) was sufficient to reveal the product as a trioxytriphenylmethane derivative. Its hydrolytic fission into di-p.-dioxybenzophenone (Liebermann), and

the proof afforded, in a similar manner, of the position of the amido groups in Rosaniline (*q.v.*), facilitated the construction of the constitutional formula, which is still adhered to, despite its inability to satisfactorily clear up certain facts.

However, whilst the study of the triphenylmethane dye-stuffs in the Rosaniline and Malachite Green groups has borne such good fruit, the technically useful results obtained in the rosolic acid group have been, and are, very small.

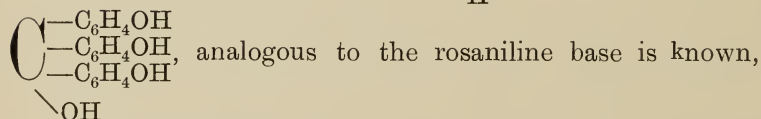
A certain confusion has arisen in the nomenclature of rosolic acid, inasmuch as the same name—rosolic acid or Aurine—is frequently applied to two different substances, whose mutual behaviour is as pararosaniline to homorosaniline.

Aurine, which on account of its analogy with pararosaniline, is also named pararosolic acid, corresponds to



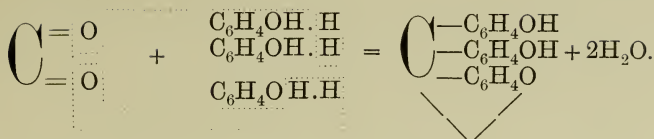
is derived from homorosaniline.

Aurine and rosolic acid are known only in this anhydrous form and as leuco compounds, $\text{C} \begin{array}{l} \text{---} \text{C}_6\text{H}_4\text{OH} \\ \text{---} \text{C}_6\text{H}_4\text{OH} \\ \text{---} \text{C}_6\text{H}_4\text{OH} \end{array}$; no carbinol,



but the triacetylaurine prepared by Herzig is a derivative thereof.

In the preparation of Aurine by heating phenol with sulphuric and oxalic acid, the latter is decomposed into carbon dioxide, which supplies the methane carbon necessary for the formation of Aurine :



Zulkowski,* who made this process the subject of special research, proved that, when pure phenol is used, the product of the reaction—crude Aurine or Coralline—also contains two additional dye-stuffs, together with two colourless isomeric substances of the composition of an oxide of Aurine. The process is still more complex when impure phenol, obtained from o. cresol, is used.

According to K. Heumann, a higher yield of Aurine is obtainable by heating phenol with carbon tetrachloride and aluminium chloride.

Probably the best method of preparing pure Aurine dye-stuffs is by the aid of formaldehyde (analogous to the new Fuchsine process).

The only use made of Aurine in dyeing is in the form of a colour lake for dyeing carpets and staining paper. Owing to its sensitivity to alkalis, it is employed—under the name of rosolic acid—as an indicator in analytical chemistry.

Aurine is poisonous.

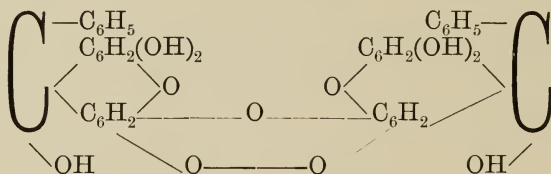
In the early days of the coal-tar colour industry, Marnas of Lyons prepared dye-stuffs by heating Aurine with ammonia and aniline, and these products enjoyed considerable vogue for some time. The product in question is termed Peonine or Red Coralline, and probably consists of rosolic acid, formed by the partial substitution of amido groups for the hydroxyls of Aurine. It is also named Coralline, for short, and is still used, to a restricted extent, for the production of a very bright red in cloth printing.

* *M. f. Ch.*, 1895, pp. 358-403 ("The Chemistry of Coralline and Fuchsine").

The **Azuline** produced by heating crude Aurine or yellow Coralline with Aniline, is a very impure Rosaniline Blue, and has gone out of use.

Latterly, certain red dye-stuffs, called **Rhodazines**, have been prepared by J. Ville, by the action of phenylhydrazine on rosolic acid; but these have no technical importance.

After a prolonged period of inanition in the development of the rosolic acid group, Doebner, in 1878, produced dye-stuffs, to which he gave the name benzeines, by the condensation of benzotrichloride with phenol, cresol, pyrogallol, naphthol, etc. They probably also belong to the same group; but exhibit certain similarities with the group of Phthaleines described later on. To the dye-stuff obtained with pyrogallol, Doebner ascribed the formula:—



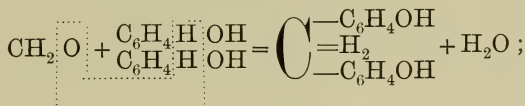
The Benzeines have no technical importance.

The experience gained with the phthaleines, namely, that alkylated and benzylated metamidophenols give with aldehydes dye-stuffs of stronger tinctorial power than are obtainable from phenols, was recently applied by K. Heumann and H. Rey to the benzenic group. As a matter of fact, they obtained dye-stuffs of far stronger tinctorial power than the Benzeines, and also possessing the property of fluorescence. To these dye-stuffs the name of Rosamine (M. L. Br.'s Rosindamine).

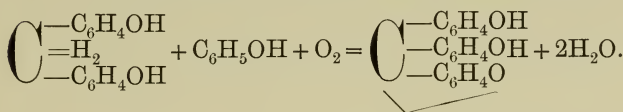
According to the researches of Biehringer,* the Rosamines belong to the Pyronines (see later).

* *Journ. f. prakt. Chem.*, vol. liv. (N.S.), p. 250.

Technical progress seems also to have been made in this branch of late by the production of Oxyaurines and Aurine carbo acids. These compounds are obtained by the condensation of formaldehyde with phenols and oxyacids, after the manner of the New Fuchsine process, *e.g.* :—

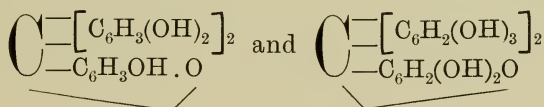


Formaldehyde. Phenol. Dioxydiphenylmethane.



Aurine.

In this way, N. Caro prepared with pyrocatechin and pyrogallol the compounds :—



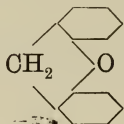
and R. Geigy, of Basle, obtained, with the aid of salicylic acid, the little used Chrome Violet, $\begin{array}{|c|} \hline \text{C} \begin{array}{|c|} \hline \text{C}_6\text{H}_3\text{COOH} \\ \hline \end{array} \\ \hline \text{C}_6\text{H}_3\text{COOH} \cdot \text{O} \\ \hline \end{array}$, which

is identical with Bayer's Chromerubine. They are all mordant dye-stuffs, whereas the Resaurine, prepared from resorcine by Nencki and Schmidt, lacks this property.

Numerous trials have latterly been made with the condensation of oxalic acid by resorcine. The course of the reaction depends entirely on the prevailing conditions, but the resulting yellow dye-stuffs are devoid of any technical value.

XANTHENE DYE-STUFFS.

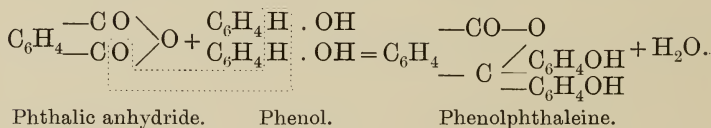
This generic term is applied to several groups of dye-stuffs, all the members of which are derived from xanthene :



and include the Phthaleines (Eosine, Rhodamine, etc.), Pyronines, Succineines, Sacchareines, and Sulphureines.

THE PHTHALEINES.

Ad. Baeyer found (1871) that when phthalic anhydride is heated with phenol in presence of a hygroscopic substance (zinc chloride, sulphuric acid, tin tetrachloride), the two condense to a product, the method of formation and constitution of which may be expressed by the equation :



This product, phenolphthaleine, is the first representative of a whole group of compounds, to which the name Phthaleines has been given.

With some phenols the combination with phthalic anhydride occurs in a manner analogous to the formation of phenolphthaleine, on exposure to a temperature of 100-120° C. in presence of hygroscopic substances. For example,

CH₃¹

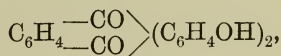
o. cresol and orcinol behave in this manner, C₆H₃OH³; other

OH⁵

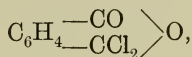
phenols combine with phthalic anhydride on being simply

heated to 200° C., without the necessity for any hygroscopic substance ; to this class belong resorcline and pyrogallol.

That phenolphthaleine—and the other phthaleines also—has an asymmetric constitution, and is not composed in accordance with the formula

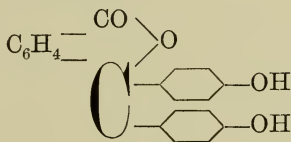


is concluded from the circumstance that phthalyl chloride, which is also asymmetric, according to the formula

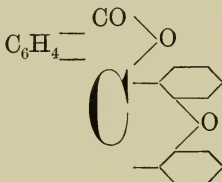


is also capable of forming phthaleine, a substitution of the two chlorine atoms occurring in the process.

The condensation between phthalic anhydride and phenol goes on in the para position of the two phenol molecules. To a small extent a subsidiary ortho condensation also occurs, the result of which, however, is not a true phthaleine, but an anhydride :



Phenolphthaleine.

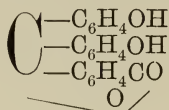


o. Phenolphthaleine anhydride.

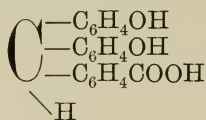
The general rule is that only such phenols as contain unoccupied para positions furnish true phthaleines, those with the para positions occupied giving anhydrides. Thus, for example, o. cresol gives a true phthaleine, but p. cresol an anhydride. Grabowski obtained an α -naphtholphthaleine from phthalic chloride and α -naphthol ; β -naphthol, on the other hand, does not furnish a phthaleine.

A closer examination of the formula of phenolphthaleine will reveal that it is also a triphenylmethane derivative, and,

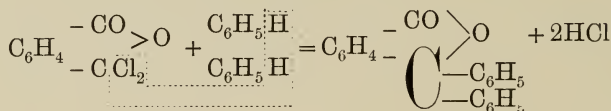
in fact, may be regarded as the anhydride of a dioxytriphenylmethane carbo acid, corresponding to the formula :—



Consequently, the phenolphthaleine formed by the reduction of an alkaline solution of phenolphthaleine with zinc, would, therefore, be entirely analogous to the leuco bases of the triphenylmethane dye-stuffs, and would have the formula :—

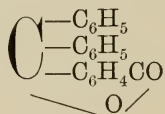


The fundamental triphenylmethane carbo acid has been isolated by Fridel and Crafft's, by heating phthalyl chloride with benzol in presence of aluminium chloride, and has received the name of phthalophenone :



Phthalophenone.

or, if written as a triphenylmethane derivative :—



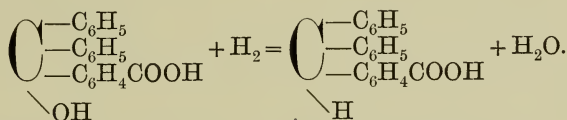
Phthalophenone is a simple phthaleine, and consequently the other phthaleines must be regarded as its derivatives. Hence, phenolphthaleine is a dioxyphtalophenone, as has also been proved by the introduction of two hydroxyl groups into phthalophenone.

When phthalophenone is treated with concentrated nitric acid, a dinitro derivative is formed ; this furnishes, on re-

duction, a corresponding diamido compound ; and on treating this with nitrous acid and boiling the product with water, phenolphthaleine is obtained.

The aforesaid close connection between the phthaleines and the triphenylmethane derivatives has also been demonstrated by the conversion of phthalophenone into triphenylmethane.

If phthalophenone be heated with alcoholic potash, it is converted into the potassium salt of an unstable triphenylcarbinol carbo acid ; this, on being treated with zinc in an alkaline solution, furnishes the corresponding triphenylmethane carbo acid :



Triphenylcarbinol carbo acid. Triphenylmethane carbo acid.

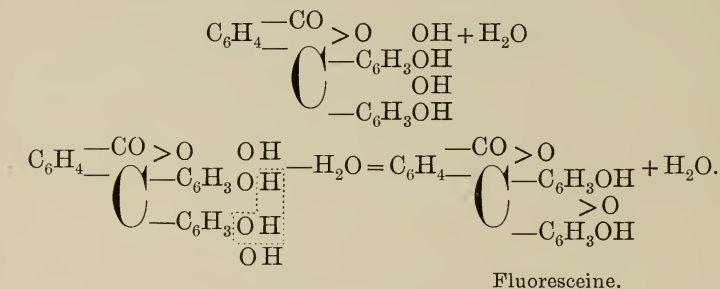
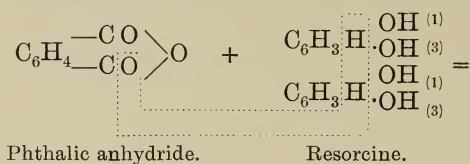
The latter furnishes triphenylmethane when subjected to dry distillation.

Phenolphthaleine itself is not a dye-stuff, and is only used as an indicator in analytical chemistry, the beautiful red colour it gives in alkaline solutions being entirely destroyed by the slightest excess of any acid. It is also suitable for titrating coloured liquids (in which case the other indicators cannot be used, *e.g.*, solutions of crude cream of tartar). Like litmus, it is sensitive to carbonic acid.

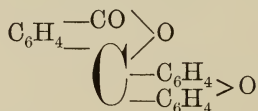
A phenolnaphthaleine is obtained by heating naphthalic acid (naphthalene- 1. 8.-dicarbo acid) with phenol and aluminium chloride.

The first dye-stuff of this group was prepared by heating phthalic anhydride to 200° C. with resorcine (Baeyer). In this reaction there is formed at first a condensation product from 1 molecule of phthalic anhydride and 2 molecules of

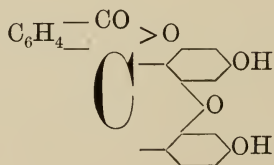
resorcine, but this is instantly converted, by intramolecular elimination of water, into the actual dye-stuff Fluoresceine :



Similar internal condensation products also occur with the other phthaleines, so that, in accordance with the proposition of Richard Meyer, the body

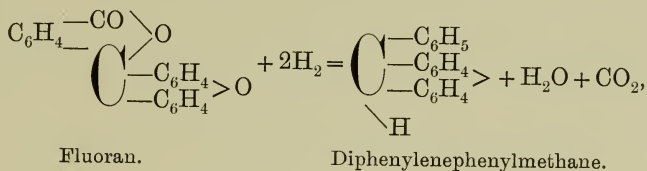


may be regarded as the fundamental substance of the dye-stuffs of this group. We have already become acquainted with a substance of this composition in the o. phenolphthaleine anhydride obtained as a by-product in the preparation of phenolphthaleine. Meyer proposed to call it Fluoran, in order to indicate its near connection with Fluoresceine and the dye-stuffs derived from this latter. According to this idea, Fluoresceine would be a dioxyfluoran of the following constitution :—

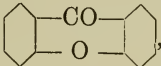


though it still remains to be proved whether, in the formation of Fluoresceine, the intrusion of the phthalic anhydride really occurs in the para position to one, and the ortho position to the other, of the hydroxyl groups of the resorcine. That this is so will be shown in the case of Eosine.

By distilling Fluoran with zinc dust and soda-lime, R. Meyer obtained diphenylenephenylmethane :



which circumstance—taking as proved the aforesaid intimate connection between Fluoran and Fluoresceine—affords an additional proof of the near alliance of the phthaleines with the triphenylmethane derivatives.

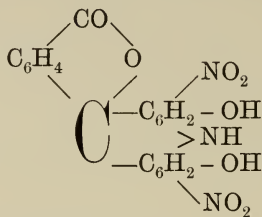
When Fluoran is distilled with lime it is decomposed into xanthone, , and benzoic acid, (C₆H₅COOH).

Fluoresceine dissolves in alkalis, the solution being of a reddish-yellow colour with beautiful pale green fluorescence, a property to which it owes its name. The tinctorial power of such a solution is extremely great, 2-3 parts of Fluoresceine being sufficient to impart a decided green fluorescence to 1,000,000 parts of water. As a dye-stuff it has no value when used alone, its dyeings being too fugitive ; but recently the potassium (or sodium) salt has been introduced, under the name Uranine, for the production of brilliant yellow shades in dyeing silk and printing wool.

When treated with reducing agents, Fluoresceine is converted into the colourless Fluoresceine, just as phenolphthaleine is changed into a leuco derivative.

By the action of ammonia on dinitrofluoresceine, Rever-

din obtained a pure yellow dye-stuff, said to be faster than Fluoresceine; it probably has the following composition:—



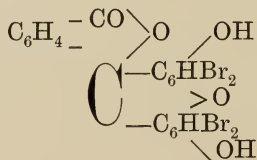
Gilliard, Monnet and Cartier have prepared sulphured fluoresceines; thus, when dichlorofluoresceine is treated with sodium sulphide, there results a dye-stuff, the bromine and iodine derivatives of which dye violet (Cyclamines).

A Naphtholfluoresceine (By.) has been prepared from 1. 3. dioxynaphthalene, but is devoid of any technical value.

Far more important than Fluoresceine itself are the dye-stuffs derived, and in part prepared, from this substance. These may be grouped under the name Eosines, and will now be described.

It was found by H. Caro in 1874 that Fluoresceine is readily capable of absorbing bromine, and thereby becoming converted into a red dye-stuff, to which its discoverer gave the name of Eosine (*Eos*, day-blush), on account of the brilliant beauty of its dyeings on silk. Notwithstanding its initially very high price—about £20 per lb.—it immediately found employment for dyeing silk. At the same time, it led the way to the production of a whole series of dye-stuffs, all of them characterised by incomparable beauty and fluorescence, but deficient in fastness.

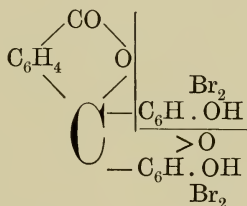
Eosine is tetrabromofluoresceine, and has the formula:—



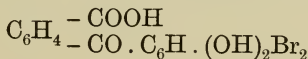
or rather the potassium salt of this compound, and is prepared by dissolving Fluoresceine in caustic soda, treating the solution with the necessary calculated quantity of bromine, also dissolved in caustic soda, and then acidifying the mixture, whereupon the sparingly soluble Eosine is precipitated. Other products, containing less bromine, are prepared, and the yellowness of shade is inversely proportional to the amount of bromine present. This is easy to understand when it is remembered that it is owing to the introduction of bromine into the molecule of Fluoresceine that the yellow colour of the latter is changed into red.

According to a Patent Specification, Fluoresceine can also be halogenised by the aid of the electric current.

The position of the hydroxyl groups and the bromine atoms in Eosine is determined in the following manner: By splitting up the molecule of Eosine with boiling caustic soda, in the direction shown by the line drawn through the subjoined formula:—

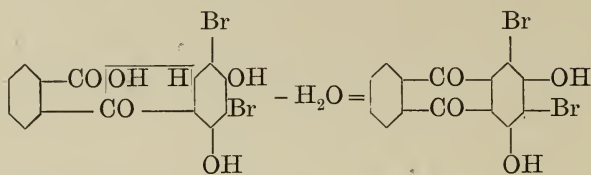


A. Baeyer produced a dibromodioxymethylbenzoic acid,



in which the hydroxyl groups and the bromine atoms must necessarily have the same position as they occupy in Eosine. Recently, G. Heller has succeeded in decomposing this acid, with elimination of water (by the acid of fuming sulphuric acid), into a known dibromodioxanthraquinone (dibromoxanthopurpurine), which only appears possible, provided the

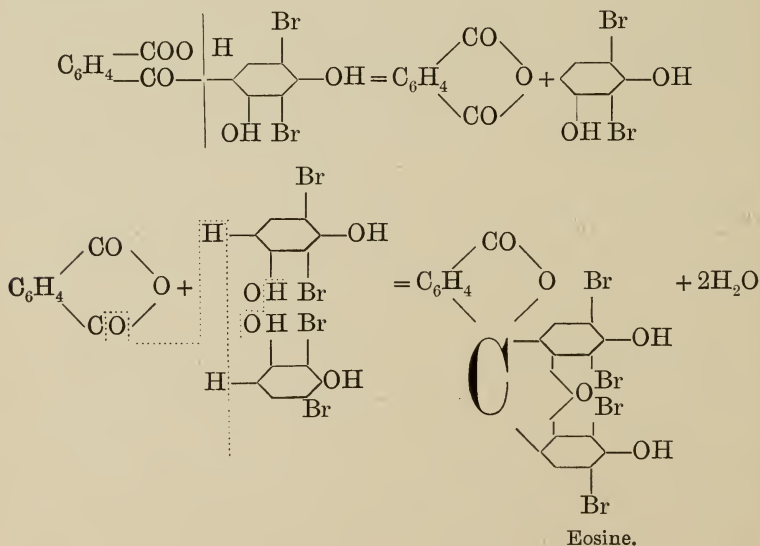
hydroxyl groups and the bromine atoms have the following position :—



Dibromodioxylbenzoylbenzoic acid.

Dibromoxanthopurpurine.

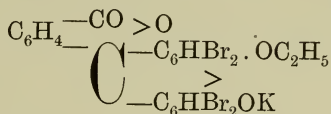
This, however, only proves the constitution of the one resorcine radicle, which has been eliminated from the Eosine, by alkali, as dibromodioxylbenzoylbenzoic acid. That the second resorcine radicle must also have the same constitution has been demonstrated by Richard Meyer, by means of a simple and elegant experiment. He heated the above-named dibromodioxylbenzoylbenzoic acid to a temperature above its melting point, and thereby obtained phthalic acid and Eosine, the formation of which can be seen from the equations :—



Of course, this also demonstrates the position of the hydroxyl groups in fluoresceine.

Still more handsome, and at the same time faster, than Eosine are its ethers, *e.g.* :—

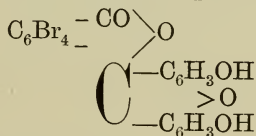
Spirit Eosine, Eosine S, Primrose, etc., the potassium salt of tetrabromofluoresceine ethyl ether, corresponding to the formula :—



Eosine Scarlet, Eosine BN, Safrosine, is the sodium salt of a dibromodinitrofluoresceine.

Erythrosine, Soluble Primrose, etc., is the iodine derivative of Fluoresceine corresponding to Eosine.

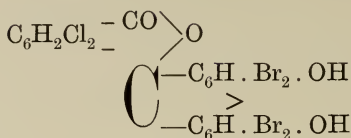
If the preparation of Eosines be undertaken from dichlorophthalic acid, the products are of bluer tinge and handsomer than the Eosines themselves. E. Noelting was the first to make them in this way. A fact of theoretical interest in this connection is that the introduction of chlorine or bromine into the phthalic acid radicle of Fluoresceine does not effect the alteration in the properties of the resulting dye-stuff nearly so well as substitution in the resorcine radicle. Thus, for instance, Eosine differs fairly considerably in properties from its parent substance Fluoresceine, whereas the tetrabromofluoresceine from tetrabromophthalic acid,



is very similar to Fluoresceine.

The following are the most important dye-stuffs of this class :—

Phloxine is the potassium salt of dichloroeosine, *i.e.*, a dichlorotetrabromofluoresceine, of the formula :—



Its methyl and ethyl ethers are called Cyanosine.

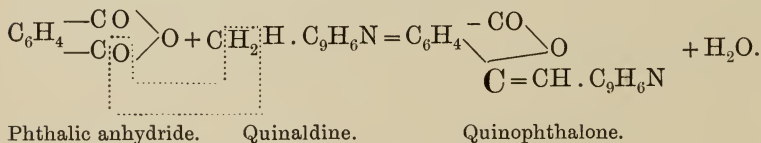
Rose Bengale is the tetraiodine derivative corresponding to Phloxine. It, therefore, stands in the same relation to Phloxine as Erythrosine does to Eosine. It is a beautiful bluish-red dye-stuff.

The Eosines are acid dye-stuffs, largely used for the production of delicate rose red dyeings, chiefly on silk. Latterly they have also been applied to wool, and for calico printing, being, in the latter case, advantageously fixed with chrome, according to the recommendations of the Farbwerke, form. Meister, Lucius and Brüning. They, therefore, possess the property of forming colour lakes with mordants, for which purpose they are now chiefly used. Their dyeings on silk exhibit fluorescence.

Somewhat different in tinctorial properties and constitution is a yellow dye-stuff belonging to this class, *viz.* :—

Quinoline Yellow.—On condensing phthalic anhydride with quinaldine (α -methylchinoline  in presence

of zinc chloride, there is formed a yellow dye-stuff, soluble only in alcohol, namely, Quinophthalone :



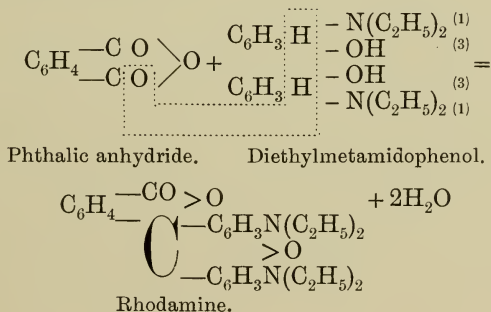
The sodium salt of the disulphonic acid of Quinophthalone is put on the market as Quinoline Yellow, and forms a highly prized yellow acid dye-stuff, since of all its compeers it gives the purest green-tinged shades, and is particularly fast to

light. Notwithstanding its high price, it is largely used in dyeing wool and silk.

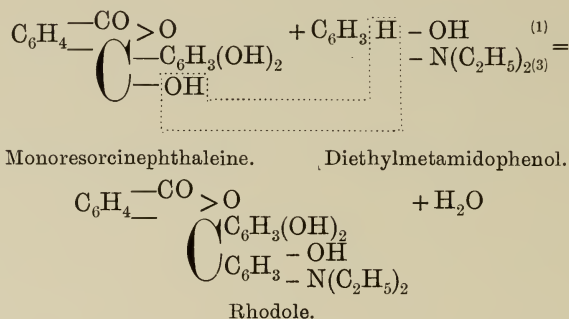
RHODAMINES.

After a long period of stagnation in the further extension of the Eosine group, it was discovered in the laboratory of the Badische Anilin- und Sodafabrik that metamidophenoles, also, are capable of condensation with phthalic acid, and that this method furnishes dye-stuffs which are quite as handsome as the Eosines, and of greater fastness and tinctorial power. Furthermore, in contrast to the acid Eosines, they exhibit a basic character, and can, therefore, serve for dyeing tannined cottons. The first member of this class was put on the market by the above-named firm in 1887, under the appellation of Rhodamine. Its appearance excited attention, and met with a cordial reception from cotton dyers, since it enabled them to produce a handsome rose red on cotton, with the aid of tannin—or still better, with Turkey Red oil and aluminium acetate as fixing agents; whereas hitherto they had been obliged to content themselves with the unpractical lead lake of Erythrosine. Subsequently, Rhodamine also proved itself a valuable dye for wool and silk.

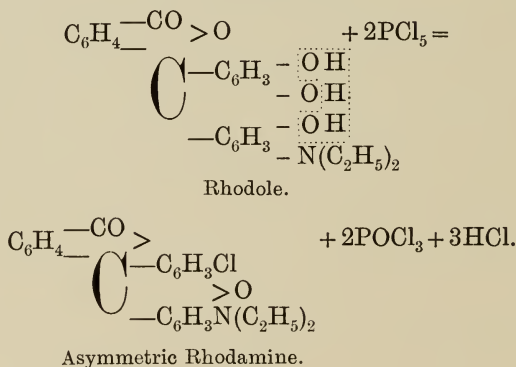
The formation of this dye-stuff can be expressed, in a manner analogous to the already mentioned phthaleines, by the following equation:—



A series of compounds, occupying an intermediate position between Fluoresceinephthaleine and the Rhodamines, has also been prepared, and to these the name **Rhodole** has been given, *e.g.* :—



Of themselves these compounds have no practical importance ; but, when treated with phosphorus pentachloride, they are transformed into asymmetric Rhodamines, which possess valuable tinctorial properties.



It was also found practicable to combine phthalic anhydride with only a single molecule of dialkyl m. amidophenol ; the resulting colourless amido acids can be condensed with a second molecule of an amidophenol, thus enabling asymmetric Rhodamines to be obtained : Rhodine (Bindschedler), Irisamine (Cassella).

If, in the foregoing reaction, the dialkylated *m.* amido-phenol be replaced by tetralkylated metaphenylenediamine, or *m.* oxydiphenylamine, dye-stuffs similar to Rhodamines are also obtained.

From the Rhodamines themselves a number of dye-stuffs have been prepared by various methods, but only very few are in use. Rhodamine sulphonic acids have been produced, containing sulpho groups either in the phthalic acid radicle, or in the other nuclei. To this class belongs Fast Acid Eosine G (M. L. Br.).

In addition to nitrated Rhodamines, dye-stuffs have also been prepared by acting on Rhodamine with amines, hydrazines, phenols, etc.; it would appear that, in these cases, the reaction occurs in the lactone ring. On eliminating alkyl groups from Rhodamine by heating along with acids, the products obtained are—like those resulting from oxidation—Rhodamines of a yellower tinge, *e.g.*, Rhodamine G (triethylrhodamine). Alkalis cause the elimination of amido groups from the Rhodamines, and furnish acid dye-stuffs which can also be fixed with mordants. Finally, the Rhodamines also yield esters, which are distinguished from the parent substance by their yellower tinge and greater affinity for textile fibres, cotton in particular. This class includes Monnet's Anisoline (Gilliard, Monnet & Cartier), Rhodamine 6G (B. A. S. F.) and others.

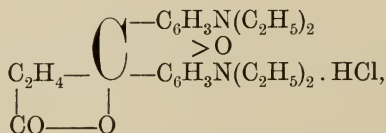
Proceeding from the synthetical preparation of Rhodamine from Fluoresceine chloride and diethylamine, the Farbwerke (M. L. Br.) investigated the influence of aromatic amines, such as aniline, toluidine, etc., on Fluoresceine, and thus arrived at a series of valuable phenylated Rhodamines, which have been put on the market partly as such, and partly in the form of sulpho acids (or the sodium salts of the latter). To this class belong the different Violamines, Fast Acid Blue R (Violamine 3D), the first blue Rhodamine,

Fast Acid Red A, and various marks of Fast Acid Violet (A, R, 2R and B), all of them produced by the above firm. These Rhodamines belong to the faster acid dye-stuffs, and, by reason of their excellent equalising properties, are of great value in wool dyeing, besides being superior to Rhodamine for silk.

Of the newer Rhodamines may be mentioned the very yellow-tinged Rhodamine 6G (see later), Rhodamine 4G (M. L. Br.), and Irisamine (C.), the two latter being distinguished by the great purity and washing fastness of their dyeings.

SUCCINEINES.

In speaking of the phthaleines from dichlorophthalic acid, it was stated that the tinctorial character of these substances is but slightly influenced by substitution in the phthalic acid radicle. From this remark the conclusion might be drawn that this portion of the phthaleine molecule has no influence on the tinctorial character of the whole; a view that finds confirmation in the fact that other dibasic acids—like succinic acid, malic acid, citraconic acid, etc.—capable of forming anhydrides, are also in a position to furnish phthaleine-like dye-stuffs. Thus Baeyer obtained Succineine by condensing succinic anhydride with resorcine; if, in this reaction, the resorcine be replaced by dialkylated meta-amidophenol, the resulting product is Rhodamine S (By.):



which has the property of dyeing cotton without the aid of fixing agents.

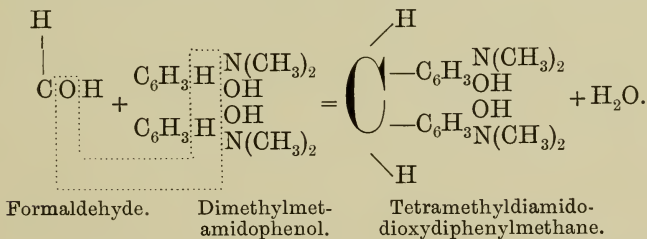
The author prepared Pyrogallosuccineine by condensing

succinic anhydride with pyrogallol. This product is a violet mordant dye-stuff exhibiting the greatest similarity to Galleine (see later).

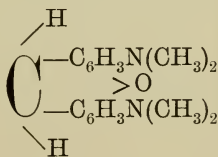
The Succineines give duller dyeings than the Phthaleines.

PYRONINES, SACCHAREINES, SULPHUREINES.

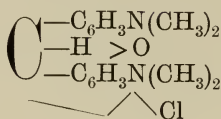
Monobasic acids, also, such as formic, acetic, benzoic, and other acids, are capable of producing dye-stuffs when condensed with dialkylated metamidophenol. Dye-stuffs of this kind, from formic acid, are put on the market by A. Leonhardt & Co., under the name Pyronines; and the Casan Red, produced by Gerber of Basle, also appears to be of this class. As an example of their method of formation and constitution, the Pyronine produced from formaldehyde and dimethylmetamidophenol, may be considered. According to Biehringer, who has studied this reaction, these two substances unite in the normal manner, in presence of hydrochloric acid (see New Fuchsine process), to form tetramethyldiamidodioxydiphenylmethane :



On warming this product with concentrated sulphuric acid, it passes over into the anhydride :



which, on oxidation (elimination of water), furnishes the dye-stuff known as Pyronine :

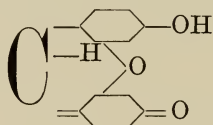


Pyronine (hydrochloride).

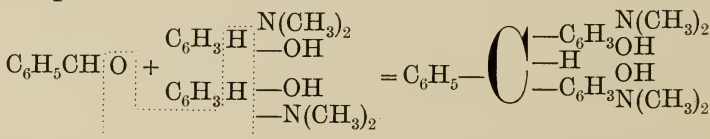
The **Pyronines** are more or less yellow-tinged red fluorescent dye-stuffs, the chief value of which is for dyeing cotton with the aid of tannin. The dyeings resemble those of Fuchsine, but exhibit greater fastness.

On oxidation the Pyronines, like the Rhodamines, are converted, with elimination of methyl groups, into dye-stuffs of a more yellow tinge.

Moehlau has prepared Pyronines containing hydroxyls in place of the amido groups ; these he terms Fluorones. To a formaldehydeoxyfluorone he ascribes the formula :—

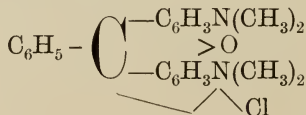


To the Pyronines also belong the dye-stuffs obtained by Fr. Bayer & Co. from benzaldehyde and dialkylated met-amidophenols :



Tetramethyldiamidodioxo-triphenylmethane.

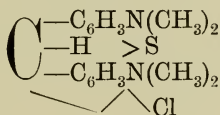
the resulting condensation product being converted, by elimination of water and oxidation, into the dye-stuff :



These products are probably identical with the Rosamines of K. Heumann and H. Rey, prepared from benzotrichloride and dialkylated metamidophenols.

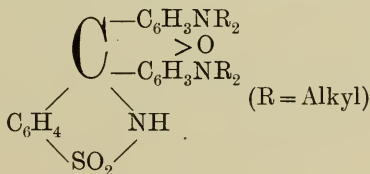
Dye-stuffs resembling Pyronines have also been prepared from chloral, by condensation with dialkyl-m.-amidophenol, leuco bases being formed at first, and afterwards converted into red dye-stuffs by oxidation and warmth. In this reaction, blue intermediate products are formed, wherein the two hydroxyl groups are probably still present; on applying heat, the Pyrone ring is formed by elimination of water.

Finally, to this group also belong the sulphurous dye-stuffs obtained by R. Geigy & Co., by the action of sulphur sesquioxide (S_2O_3) on alkylated diamidodiphenylmethane dissolved in concentrated sulphuric acid. According to the patent specification (Ger. Pat., 65,739, 20th Feb., 1892), their constitution can be represented by the following formula:—

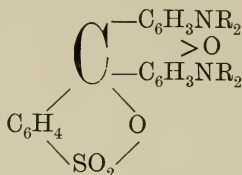


These dye-stuffs therefore differ from Leonhardt's Pyronines only in the oxygen, connecting the two aromatic nuclei, being replaced by sulphur.

By condensing saccharin, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{SO}_2 \end{array} \text{NH}$, with dialkylated m. amidophenol, P. Monnet and J. Koetschet obtained dye-stuffs similar to Rhodamines, to which they gave the name **Sacchareines**. Their composition may be expressed by the following formula:—



They are decolorised by alkalis, and are, therefore, devoid of technical value; but when the imide group therein is replaced by oxygen,

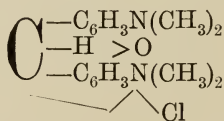


dye-stuffs perfectly fast to alkali are obtained—the so-called Sulphureines. Apparently identical with these are the dye-stuffs obtained by Geigy through the condensation of benzaldehydeorthosulphonic acid ($\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{COH}^{(1)} \\ \text{SO}_3\text{H}^{(2)} \end{smallmatrix}$) with dialkylated m. amidophenols.

RECENT VIEWS ON THE CONSTITUTION OF THE PHTHALEINES.

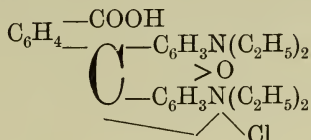
Latterly, a comparison between the formulæ of Pyronine and Rhodamine, on the one hand (Bernthsen), and the remarkable alterations of colour sustained by phenolphthaleine on entering into saline combination, on the other (Friedlaender), has led to the development of new ideas on the subject of the constitution of the phthaleines, which opinions will now be discussed.

Bernthsen regards the above-mentioned Pyronine,

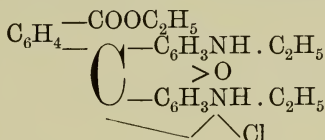


as a Rhodamine derived from formic acid, and consequently proposes to name it Formorhodamine. It may be taken to represent the simplest form of Rhodamine, from which all the others are derived by replacing the methane carbon with other radicles.

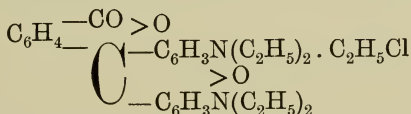
According to this hypothesis, only the colourless anhydrous Rhodamine base would exhibit the constitution given on p. 197, whilst its intensely coloured chloride must contain a free carboxyl group, in accordance with the formula :—



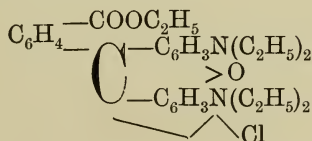
In reality, the behaviour of Rhodamine on esterification speaks in favour of the last formula; and dye-stuffs have been prepared which must be regarded as carboxyl esters of Rhodamines, such as Anisoline and Rhodamine 6G (B.) :—



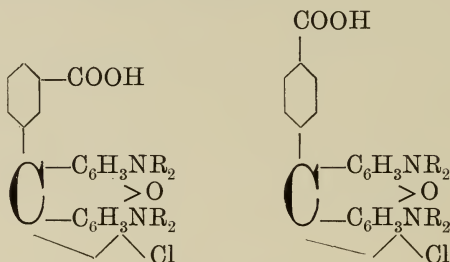
Tetralkylated Rhodamine gives with ethyl chloride an ester, which, however, is also produced when Rhodamine is treated with such reagents as act exclusively by esterification, and do not convert amines into ammonium bases; *e.g.*, alcohol and hydrochloric acid. Furthermore, under the action of the same reagents, dialkylrhodamines, instead of furnishing the stable trialkyl derivatives, give readily saponifiable esters, which, therefore, cannot have the formula



but must rather—bearing the above facts in mind—be credited with the constitution:—

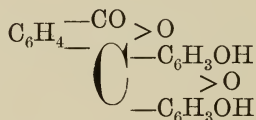


Noelting and Paira condensed nitrobenzaldehyde with dialkylated m. amidophenol, effected the closing of the pyrone ring by eliminating water from the hydroxyls, and finally displaced the nitro group by carboxyl. In this way they obtained dye-stuffs, which, in consequence of the mode of preparation, certainly contain a free carboxyl group, and are very similar to ordinary Rhodamine :—

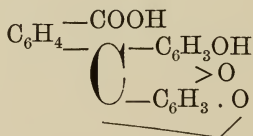


We are, therefore, justified in assuming Rhodamine to also contain a free carboxyl group, and in regarding it as a quinoid compound.

By analogy, the free Fluoresceine alone should have the lactone formula :—



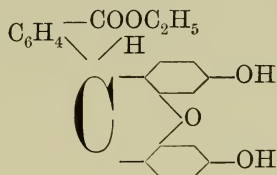
given on p. 188, whilst its salts must have the quinoid formula :—



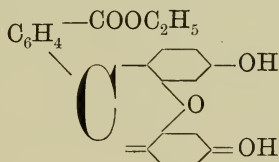
In order to decide this theoretically important question, the ether of Fluoresceine has been subjected to a very careful investigation by O. Fischer, Hepp, Nietzki, Schroeter, and others. The results showed that Fluoresceine may exist

in both the lactone and the quinoid form, the former being the more stable of the two. With regard to Eosine, Nietzki has shown the great probability of this, too, exhibiting a quinoid structure.

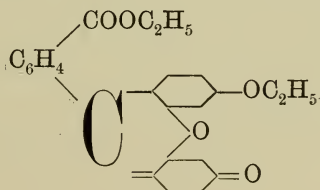
For the elucidation of this complex matter we are mainly indebted to the labours of Nietzki and Schroeter. By ethylating Fluoresceine with alcohol and hydrochloric acid, they first prepared a monoethyl ether, which, from the mode of formation, is probably a carboxyl ether:—



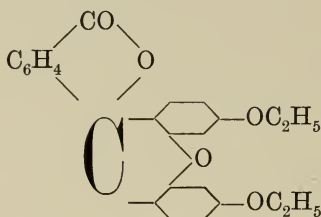
This was next oxidised to the corresponding ether of Fluoresceine, which—assuming it to be a carboxyl ether—must exhibit the following quinoid structure:—



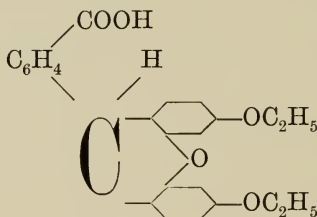
By the bromination of this product, Nietzki and Schroeter obtained an ether of Eosine, from which they conclude that the Eosines are of quinoid constitution. The further ethylation of the said quinoid monoethyl ether gives a yellow diethyl ether, insoluble in alkalis, and to which these authors ascribe the quinoid formula:—



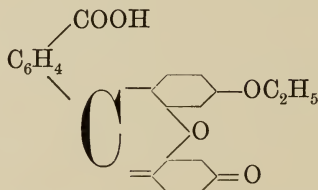
Strong support is afforded to this hypothesis by the existence of an isomeric ether, which has been proved to exhibit the lactone formula:—



It is colourless, and is converted, on reduction, into a fluoresceinediethyl ether, with a free carboxyl group:—



In addition, the quinoid nature of the coloured fluoresceinediethyl ether is indicated by the fact that it is easily saponified into a yellow monoethyl ether, soluble in alkalis, and to which, therefore, the quinoid form must also be attributed:—

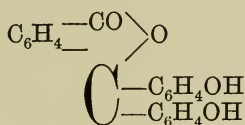


In the ethylation of Fluoresceine salts, the production of the quinoid diethyl ether is always accompanied by that of the colourless lactone diethyl ether; on benzylation in alkaline solution, a lactone ether is formed (R. and H. Meyer).

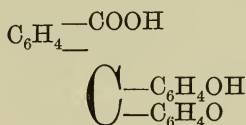
From this it must be concluded that, in the case of Fluoresceine, the lactone form is the more stable modification, whereas the converse seems the case with Eosines.

It should, however, be remarked that the proof of the existence of a quinoid form of these compounds is merely indirect; *i.e.*, what has been shown is the disappearance of a hydroxyl group and the appearance of a carboxyl group, but not the presence of a quinone oxygen.

The remarkable colour change exhibited on the conversion of the colourless phenolphthaleine into the condition of alkali salt, is also referred by Bernthsen and Friedlaender to a conversion of the colourless lactone form into the coloured quinoid form:—

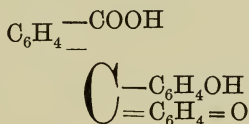


Lactone form.

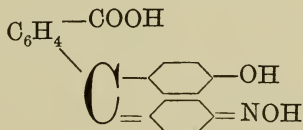


Quinoid form.

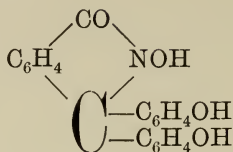
or



However, the compound of phenolphthaleine with hydroxylamine, prepared by Friedlaender, in support of this view, is not a phenolphthaleineoxime,



as was believed at first. According to Herzig and H. Meyer, the formula is probably:—



Consequently, the existence of a quinoid form of phenolphthaleine is still unproven, and, for certain reasons, is also improbable.

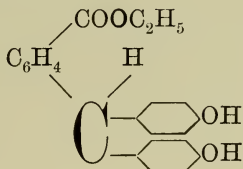
Against the assumption of a quinoid form of phenolphthaleine may be cited the fact that, both on alkylation (Herzig and H. Meyer) and on benzylation (Bistrzycki and Nenzki), in alkaline solution—in which the existence of the quinoid form has been assumed—colourless lactones are obtained. No undoubted quinoid compound of phenolphthaleine is known at all; and there is therefore no ground for supposing that the salts of phenolphthaleine should be of quinoid constitution. The colour change ensuing on treating phenolphthaleine solution with an alkali, and the behaviour of this solution in particular, can be more satisfactorily explained by assuming an ionisation, in the sense of Ostwald's theory of indicators (Herzig). When such a solution is treated with an excess of alkali, it becomes colourless, owing to a retrogression of the ionisation; on warming, the colour makes its reappearance, and disappears once more on cooling (Baeyer). An alkaline solution of phenolphthaleine can also be decolorised by alcohol (R. Meyer).

The conditions are different with regard to the bromine derivatives of phenolphthaleine, coloured ethers of which, of quinoid constitution, have been prepared by Nietzki and Burekhardt.

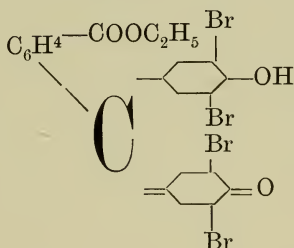
Hence, the introduction of bromine atoms increases the tendency to the formation of quinoid compounds in both phenolphthaleine and Fluoresceine. This is progressively accompanied by the appearance of tinctorial properties in

phenolphthaleine, and by a deepening of colour in the case of Fluoresceine.

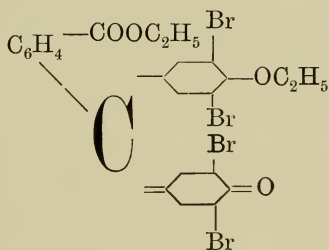
Nietzki and Burckhardt first brominated Herzig's phenolphthaleinemonomethyl ester :



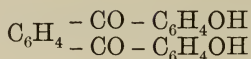
and then oxidised it to a phenolphthaleine derivative, which must apparently be of quinoid constitution :—



This product, in itself yellow, dyes silk blue, and on ethylation furnishes a tetrabromophenolphthaleinediethyl ether :



Of late, an entirely different opinion of the constitution of phenolphthaleine has been expressed by Hans Meyer, according to whom phenolphthaleine in neutral solution has the lactone form, but in alkaline solution a symmetrical structure corresponding to the formula :—



The transformation from one state to the other would consequently be effected by the migration of a phenol radicle from one carbon atom to another, which is very improbable in view of the readiness with which the colourless phenolphthaleine is converted into the coloured form by alkalis.

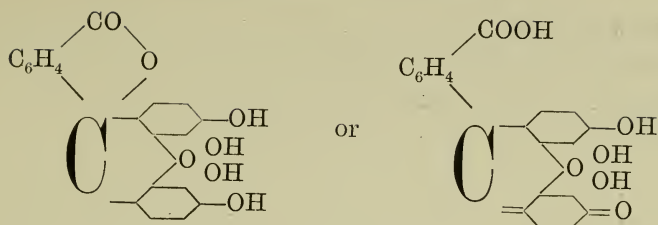
GALLEINE AND COERULEINE (BAEYER).

From the method of their preparation these two dye-stuffs also are classed along with the Phthaleines, although, in so far as their tinctorial properties are concerned, they differ somewhat considerably from the Phthaleines already described, and are more closely connected with the Alizarine dye-stuffs (see later).

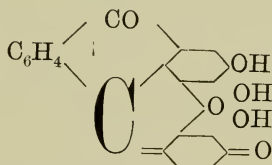
Galleine and Coeruleine are decided mordant dye-stuffs—"dye-stuffs" in the sense implied by Perger, since they can only be used in the condition of lakes.

Whereas the Phthaleines hitherto described are almost without exception red in colour, the lakes of Galleine are violet, and those of Coeruleine green. Finally, these colour lakes exhibit a fastness greatly exceeding that of the dyeings furnished by the other Phthaleines.

Galleine is formed, analogous to Fluoresceine, when phthalic anhydride and gallic acid are heated to 200° C. In this reaction, the gallic acid is decomposed into carbon dioxide and pyrogallol, which latter condenses to a dye-stuff with the phthalic anhydride. Orndorf and Brewer, who have recently repeated the older work of Buchka, on Galleine and Coeruleine, and rectified the same in some particulars, give Galleine the following formula:—



Coeruleine is obtained by heating Galleine to 200° C. with an excess of concentrated sulphuric acid. According to Orndorf and Brewer, its constitution corresponds to the formula :—



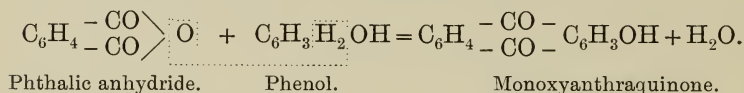
which indicates its origin from Galleine by the elimination of 1 molecule of water. Buchka constructed another far more complex formula for this substance.

Dye-stuffs similar to Coeruleine (*e.g.*, Coeruleine B (M. L. Br.)) have latterly been prepared from substituted Fluoresceines, Eosine.

Galleine is used to a small extent in dyeing the three principal textile fibres and also in calico printing, in the form of its vivid violet chrome lake ; but its chief employment is in the manufacture of Coeruleine. This latter dye-stuff is not only faster than Galleine, but is actually one of the fastest green dye-stuffs known. Its dull green chrome lake is largely used in fast-dyeing wool, silk and cotton, and also in calico printing. Like Galleine it is insoluble in water, and is generally sold as paste ; also frequently in the form of bisulphite (Coeruleine S).

The condensation of phthalic anhydride by phenols can also be effected in a manner different to that pursued in the

production of the Phthaleines. For example, if 1 molecule of phenol and 1 molecule of phthalic anhydride be heated with a large excess of concentrated sulphuric acid, the product is not a Phthaleine, but a monoxyanthraquinone :



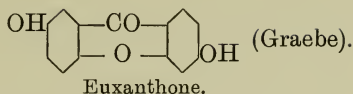
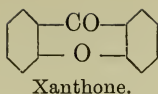
However, since this reaction leads to compounds belonging to the anthraquinone group, their description will be postponed until we come to the Alizarine dye-stuffs.

XANTHONE DYE-STUFFS.

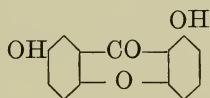
The dye-stuffs of this group have no practical importance ; their interest consists rather in the circumstance that several natural dye-stuffs belong to the Xanthoncs, and that the important group of the Flavones, to be described later on, exhibits certain analogies with the Xanthoncs.

The oldest dye-stuff of the group, and at the same time the only one in practical use, is a product known as Piuri, Purrée, **Indian Yellow**, and prepared at Monghyr (India) from the urine of cows foddered on mango leaves. The urine is collected and heated, and the deposited pigment is filtered and moulded into balls. In India this pigment is used as an artist's colour ; and it also exhibits the property of combining with mordants.

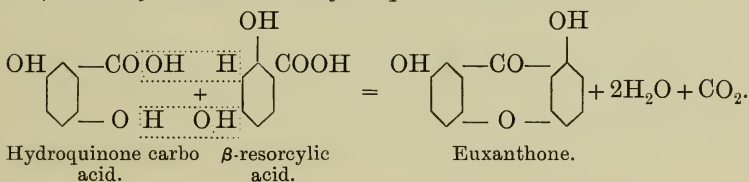
The principal constituent of Indian Yellow is the magnesium salt of euxanthic acid, a glucosidic compound, which, when treated with acids, splits up into glycuronic acid, an alcohol-aldehyde acid, and euxanthone. The last-named substance, which must be regarded as the true chromogen of Indian Yellow, is a dioxyanthone of the formula :—



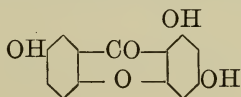
Euxanthone itself is not a dye-stuff. Its two hydroxyls exhibit divergent behaviour, inasmuch as only one of them can be easily alkylated. The resulting monoalkyl ether is yellow, and is insoluble in alkalis. The isomeric ether can only be prepared in a roundabout way; it is colourless and soluble in alkalis. This difference is probably caused by the different position of the two hydroxyl groups. It has been shown by Von Kostanecki and Dreher that, in the case of oxyxanthenes, the hydroxyl in the ortho position towards the carbonyl group is far more difficult to alkylate than another; they, therefore, ascribed the following formula to euxanthone:—



The production of this substance by artificial means, which led to the construction of this formula, was effected by Graebe, by the action of acetic anhydride on a mixture of β -resorcylic acid and hydroquinone carbo acid:—



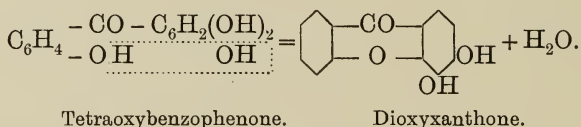
According to Kostanecki and Nessler, it can also be prepared from hydroquinone carbo acid and Resorcine; and the substitution of phloroglucine for Resorcine gives the Gentiseine first obtained by Kostanecki and Tambor. This substance is a trioxyxanthone of the formula:—



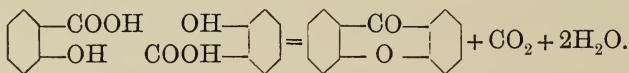
and its monomethyl ether is Gentisine, the colouring matter of gentian root. It is worthy of note that, although Gentisine contains no hydroxyl group in the ortho position, it, nevertheless, colours alumina mordants (yellow).

Datiscetine, a yellow dye-stuff occurring in the condition of a glucoside (datiscine) in the plant *Datisca cannabina*, is probably a dimethylated tetraoxyxanthone (Sckunck and Marchlewski).

Another process by which Xanthenes can be formed, and which possibly also plays a part in nature, is that from oxyketones by elimination of water. Thus the tetraoxybenzophenone resulting from the action of salicylic acid on pyrogallol, furnishes, on heating with water, a dioxyxanthone :



Xanthone itself is prepared by boiling salicylic acid with acetic anhydride :—



Latterly a series of Xanthenes, both of benzol, as well as of naphthalene and quinoline, and finally also polyxanthenes, *e.g.*, $\text{C}_6\text{H}_4 - \begin{array}{c} \text{CO} \\ \text{O} \end{array} - \text{C}_6\text{H}_4 - \begin{array}{c} \text{CO} \\ \text{O} \end{array} - \text{C}_6\text{H}_4$, have been prepared, mostly by Kostanecki.

Biehringer* obtained a tetramethyldiamidoxanthone by oxidising the corresponding Pyronine. The product is not red, as one would suppose, but yellow, dissolving to a yellow solution, with blue fluorescence, in concentrated sulphuric acid, and staining the skin yellow.

* *Journ. prakt. Chem.* (N.S.), vol. liv., p. 235.

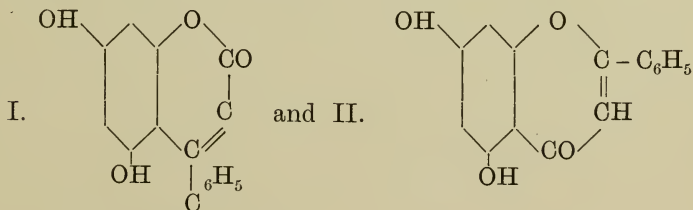
FLAVONES.

The above name was first introduced into chemical literature in 1895, being then proposed by St. von Kostanecki to denote a system of atomic grouping, which at that time was entirely hypothetic, and assumed to exist in a few natural dye-stuffs. At the present time, thanks to the labours of Kostanecki and his followers, the Flavones constitute one of the most important and interesting classes of dye-stuffs known. By special energy, Kostanecki succeeded in identifying several natural yellow dye-stuffs as Flavones, and in preparing them synthetically. It is also more than probable that most of the dye-wood pigments are either Flavones, or nearly allied thereto.

The starting-point of these researches was formed by Chrysine, a yellow dye-stuff discovered by Piccard in poplar buds, and which this worker subjected to careful experimental examination.*

Piccard found that Chrysine has the empirical formula $C_{15}H_{10}O_4$, and that, on being boiled with potash, it splits up into phloroglucine, benzoic acid, acetic acid, and acetophenone. The formation of the last-named substance was of special interest, since its appearance indicated a linking of the two radicles, benzoyl and acetyl, in Chrysine. The possibility was thus afforded of constructing constitutional formulæ for Chrysine, by means of which the said fission by alkalis can be explained.

Von Kostanecki laid down the formulæ :—



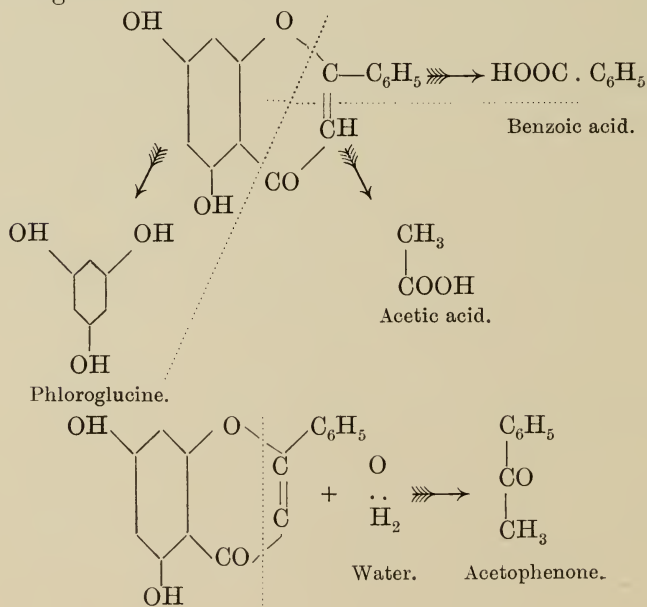
Dioxy- β -phenylcumarine.

* *Berl. Ber.*, **6**, pp. 884, 1160; **7**, pp. 888, 1485; **10**, p. 176.

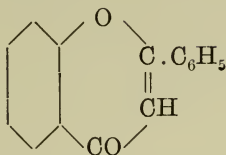
Both formulæ contain two hydroxyl groups, which stand in apparent contradiction to the fact, discovered by Piccard, that only a single hydroxyl could be detected in Chrysine by alkylation. Von Kostanecki, however, recalls the circumstance that, in the case of the Xanthones, one hydroxyl is frequently more difficult to alkylate than the others, especially those in ortho position to the carbonyl group. Similar instances of difficulty in alkylating a hydroxyl group are also confirmed by Herzig in the case of several natural dye-stuffs.

Selection between the two above formulæ was not difficult, since Kostanecki was able to show, by synthetical means, that a substance composed according to No. I. is very different to Chrysine.

The fission of Chrysine into phloroglucine, benzoic acid, acetic acid, and acetophenone, can be explained in a very satisfactory manner by formula No. II., as may be seen from the following:—



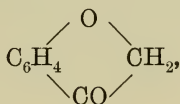
For the atomic complex



von Kostanecki proposed the name "Flavone," Chrysine being, therefore, a dioxyflavone.

The first synthetic experiments on the preparation of such Flavones were published by P. Friedlaender and his pupils. Friedlaender and Ruedt found that *o.* oxychloro (bromo) acetophenone, $\text{C}_6\text{H}_4\text{COCH}_2\text{Cl}$, or the alcohol,

$\text{C}_6\text{H}_4\text{CO}\cdot\text{CH}_2\text{OH}$, prepared therefrom by the aid of alkali, could be readily condensed with aldehydes to substances, which their discoverers at first regarded as Flavones. It was soon ascertained, however, that the products thus obtained were not Flavones, but derivatives of the body



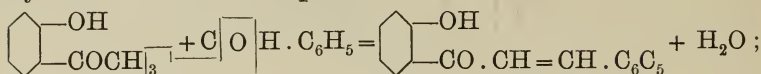
which Friedlaender named "Ketocumaran," and Von Kostanecki "Cumaranone".

Several of the hydroxyl derivatives of Ketocumaran, prepared by Friedlaender and his pupils, are yellow mordant dye-stuffs.

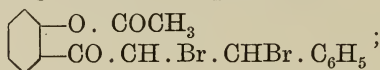
True Flavones were first produced by von Kostanecki and his colleagues, and were revealed as such by the fission effected thereon by alkalis, as already mentioned in the case of Chrysine. They further differ from the Ketocumarans by dissolving to a pure yellow solution, with blue fluorescence, in sulphuric acid, whereas the others form mostly orange yellow solutions without fluorescence.

Synthesis of Flavone.—

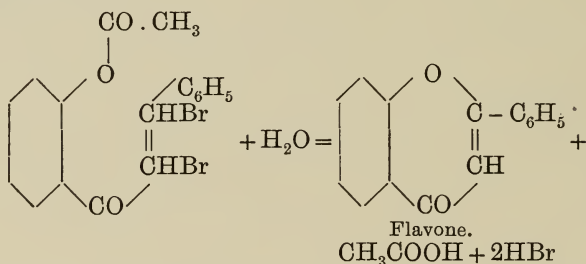
o. Oxyacetophenone is first condensed with benzaldehyde to a benzal compound:—



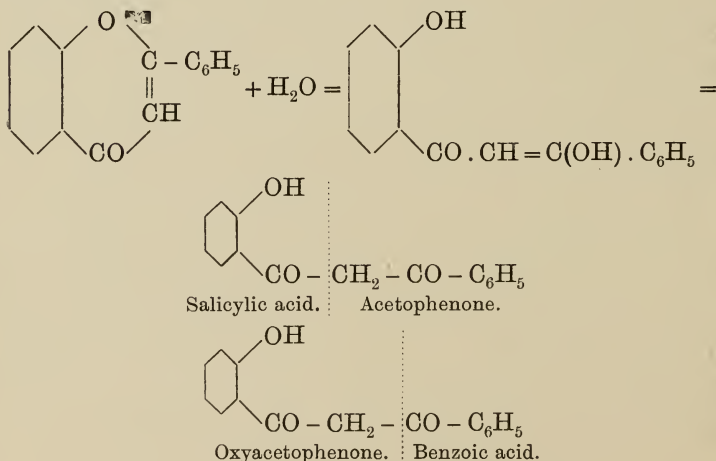
which is then acetylated, and afterwards brominated, whereupon the following substance is produced:—



and this in turn, when treated with alcoholic caustic potash, furnishes Flavone:



In the characteristic fission produced by potash, Flavone yields salicylic acid, acetophenone, oxyacetophenone and benzoic acid:—

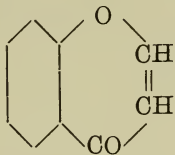


A whole series of oxyflavones are prepared in a perfectly analogous manner.

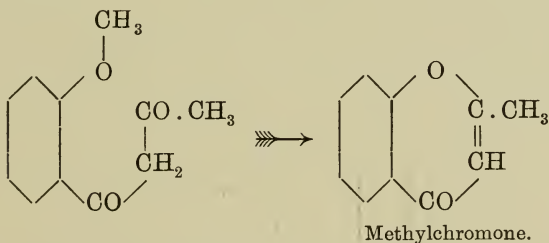
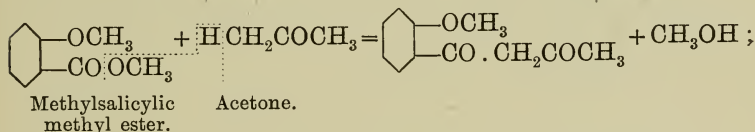
Flavone is a substance very similar to Xanthone; it forms colourless crystals, which dissolve in concentrated sulphuric acid to furnish a yellow solution with faint blue fluorescence.

Synthesis of Methylchromone.—

The atomic complex



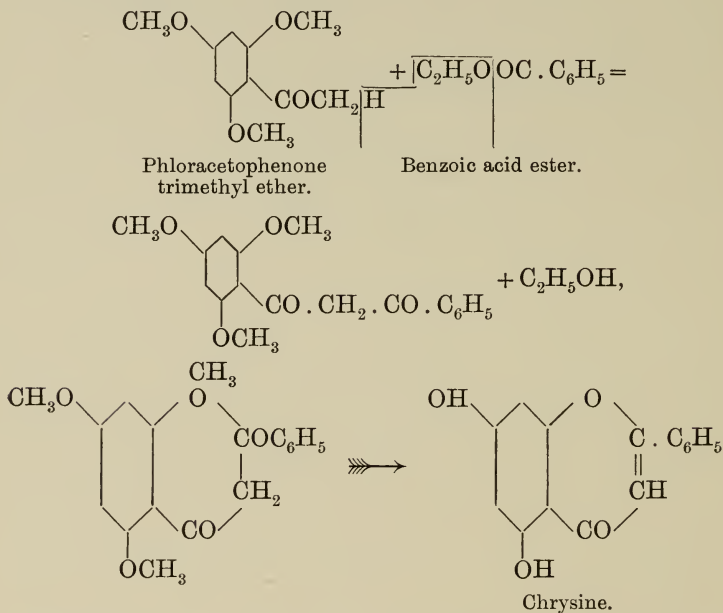
has been named "Chromone" by von Kostanecki. He prepared a methyl derivative by the following method, *viz.*, uniting methylsalicylic methyl ester with acetone to a diketone, by heating with metallic sodium, the product being then condensed with hydriodic acid to methylchromone:—



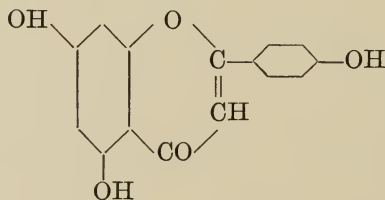
Von Kostanecki and his pupils also succeeded at length, in an entirely analogous manner, in effecting the synthesis of the three vegetable dye-stuffs, Chrysine, Apigenine, and Luteoline. In all three cases, phloracetophenone trimethyl ether is first united to a diketone by heating it with an acid

ester in presence of metallic sodium, the product being then condensed to dye-stuff by heating with hydriodic acid.

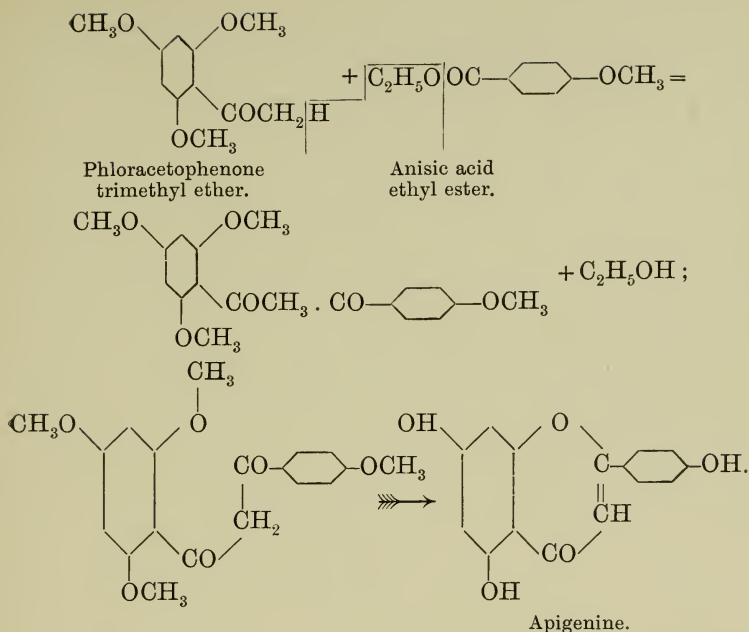
Synthesis of Chrysine (von Kostanecki, Tambor, and Emilewicz).—



Apigenine is a yellow dye-stuff obtained by decomposing the glucoside apiine occurring in parsley. A. G. Perkin identified this as a trioxyflavone and constructed the formula :—

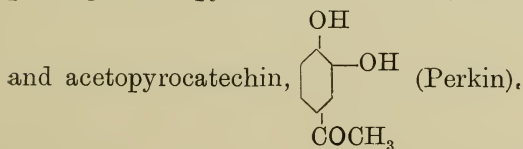


according to which view it is an oxychrysine. The accuracy of this assumption was confirmed by the synthesis of Apigenine effected by von Kostanecki, Tambor, and Czajkowski:—

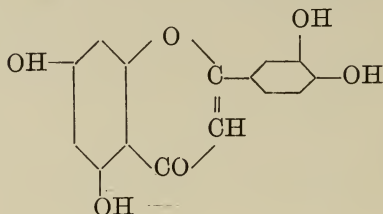


Apigenine has just as little tinctorial effect on mordants as Chrysine has.

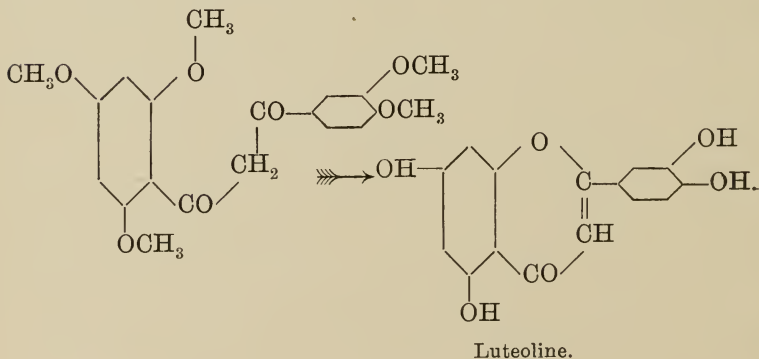
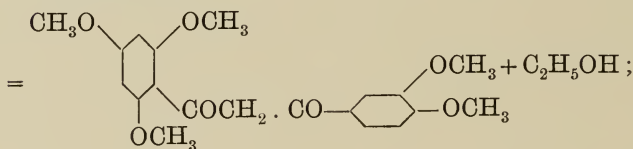
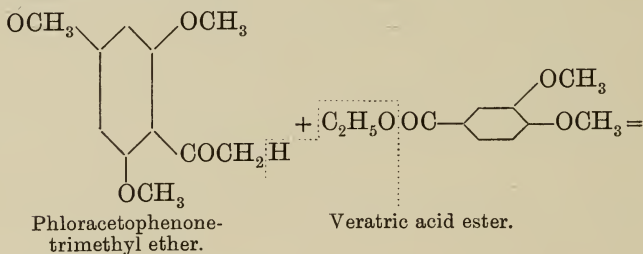
Luteoline has been investigated by a number of workers ; but we are mainly indebted to the labours of A. G. Perkin and J. Herzig for the elucidation of its constitution. Decisive information in this respect was afforded by its behaviour on alkylation, and when fused with potash. The empirical formula of Luteoline was determined as $\text{C}_{15}\text{H}_{10}\text{O}_6$ (Hlasiwetz, Pfaundler, Perkin), and it was observed to furnish, on alkylation, yellow trialkyl derivatives, which pass over into white trialkylmonoacetyl products on acetylation. This behaviour proved the presence of four hydroxyl groups in Luteoline. When fused with potash it furnishes phloroglucine, pyrocatechuic acid (Rochleder and Breuer),



On the basis of these facts, and on its similarity with the flavones, A. G. Perkin explained Luteoline as a tetroxy-flavone, and gave it the following formula:—



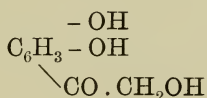
The accuracy of this formula was only recently confirmed by the synthesis of Luteoline, effected by von Kostanecki, Tambor, and Rozycki:—



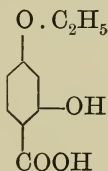
At the present time, the following dye-stuffs, occurring in the technically important dye-woods, are classed with the Flavones: Fisetine, Quercetine, Rhamnetine, and Morine.

Of these, **Fisetine** has received the greatest share of attention. For the elucidation of its constitution we are chiefly indebted to Herzig, who succeeded in effecting the fission of Fisetine by alkalis in such a manner that a constitutional formula could be at once constructed from the fragments. When fused with potash, Fisetine is decomposed into resorcine and protocathecuic acid; but if tetraethylfisetine be boiled with alcoholic potash, the fusion is less extensive, and furnishes, in addition to diethylprotocatechuic acid, the ethyl ether of a substance which Herzig named "Fisetol," and the examination of which contributed to the elucidation of the constitution of Fisetine.

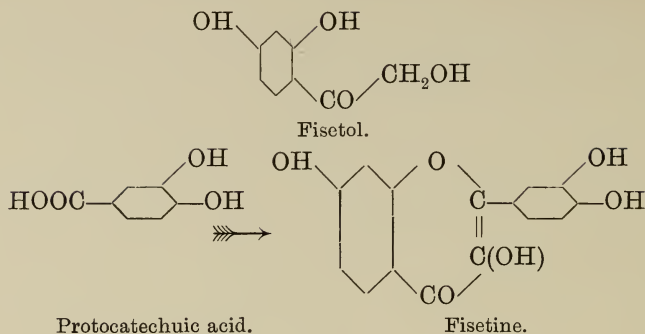
Fisetol was identified as a resorcine derivative, of the following composition:—



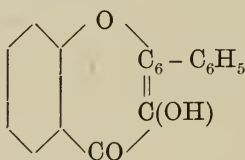
The position of the group $\text{CO} \cdot \text{CH}_2\text{OH}$ was determined by von Kostanecki, who identified an acid, obtained on the oxidation of ethylfisetol, with the ether of β -resorcylic acid:—



Finally, the analogy between Fisetine and Chrysine led to the construction of a flavone formula for the former, which was easily accomplished from the fragments by that time accurately known (von Kostanecki):—



In accordance with this conception, Fisetine appears as a trioxy derivative of the body



to which von Kostanecki has given the name "Flavonol".

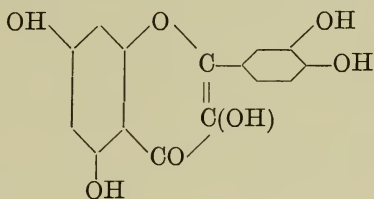
Quercetine has received special attention at the hands of research chemists; and a great deal of very careful work has been done by Hlasiwetz and Pfaundler, Liebermann, Herzig, A. G. Perkin and others in endeavouring to elucidate the constitution of this important vegetable dye-stuff.

The chief difficulties were encountered in determining its empirical composition and the number of the hydroxyl groups contained in the molecule; a problem mainly solved by Liebermann, Herzig, and A. G. Perkin. Valuable assistance in this connection was afforded by the definitely crystalline compounds—discovered by Perkin—furnished by Quercetine with mineral acids.

On alkylation, Quercetine furnishes tetraalkyl ether, in which a free hydroxyl group can be detected by acetylation. Here also the same peculiarity with regard to the difficulty of acetylating one of the hydroxyl groups is encountered, as in the case of the oxyxanthenes, and the cause may again be

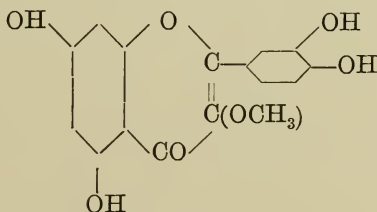
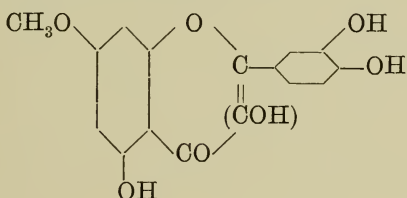
attributed to the ortho position of a hydroxyl group in relation to the carbonyl group.

Quercetine differs from the Xanthonenes by the ease with which it is split up by alkalis, protocatechuic acid and phloroglucine being obtained. The close connection between Quercetine and Fisetine—according to Herzig, Quercetine is an oxyfisetine—and the elucidation of the constitution of Fisetine, finally led to the construction of a constitutional formula, according to which Quercetine is a tetroxyflavonol:—

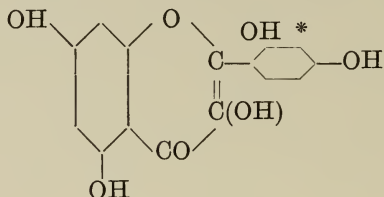


Quercetine.

Rhamnetine, which has been more particularly investigated by Liebermann, Hoermann and Herzig, has been identified by the last-named worker as a monomethylquercetine. Fused with potash, it furnishes protocatechuic acid and phloroglucine, and is probably constituted in accordance with one of the following formulæ:—



Morine, a body very similar to the isomeric Quercetine, furnishes phloroglucine and β -resorcylic acid when fused with potash, and is regarded by A. G. Perkin and Bablich as a flavonol derivative of the following constitution:—



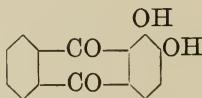
To the Flavonol group also belong the following vegetable dye-stuffs: Isorhamnetine (quercetine monomethyl ether), Rhamnazine (dimethylquercetine), Myricetine (oxyquercetine), and Camphoride[†] (dioxymethoxyflavonol).

OXYKETONE DYE-STUFFS.

Group I. Alizarine Dye-stuffs. II. Oxyketone Dye-stuffs of Divergent Constitution.

I. ALIZARINE DYE-STUFFS.

Without exception, all the older dye-stuffs of this group are hydroxyl derivatives of anthraquinone or anthraquinoline; they all contain at least two hydroxyl groups, which, according to the law established by Liebermann and Kostanecki, must be in the same position as in Alizarine,



i.e., in the ortho position to each other, as also to one of the

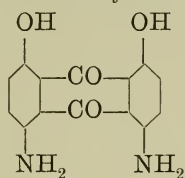
* See Herzig, *M. f. Chem.*, 1897, p. 702.

† Gordin, *Dissertation*. Berne, 1897.

two quinone groups. Other oxyanthraquinones, wherein this does not occur, are not mordant dye-stuffs.

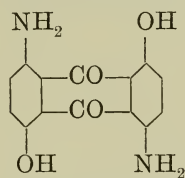
At the present time, this law is restricted to such anthraquinone derivatives as contain only hydroxyl groups, as may be seen from the following examples :—

Diamidochrysazine.



Colours mordanted and unmordanted
wool blue.

Diamidoanthrarufine.



Does not dye wool.

Recently, amidised dye-stuffs of this group have been prepared, containing no hydroxyl groups at all. These are incapable of forming lakes with mordants.

The Alizarine dye-stuffs are mostly mordant dye-stuffs, partly also acid dye-stuffs, and are distinguished by special fastness; in fact, they are classed among the fastest of all dye-stuffs.

With the exception of their sulpho acids and bisulphite compounds, as well as a few of the nitro compounds, they are all insoluble in water, and are, therefore, generally sold in the form of paste (mixed with water), though, to some extent, in the state of dry insoluble alkali compounds.

Alizarine itself, and a few of its more nearly allied members of the group, are true “dye-stuffs” in Perger’s sense; others, such as Alizarine Blue, occupy an intermediate position between “dye-stuffs” and “dyes”.

The most important member of the group, both theoretically and practically, is Alizarine itself. It occurs in nature as a glucoside, in the roots of the madder plant, *Rubia tinctorum*. This substance, also known as ruberythric acid, decomposes into Alizarine and a sugar when boiled with

acids. The practical value of the madder plant, however, has been reduced to a minimum by the preparation of Alizarine by artificial means. All further particulars on this point will be discussed in dealing with madder; for the present, all that need be stated is that, on account of its content of Alizarine, madder has been used in dyeing from time immemorial, and has played one of the principal parts in that industry. Consequently, Alizarine can be classed along with the oldest of the dye-stuffs.

At the time when chemists began to devote attention to Alizarine, it was regarded as a derivative of naphthalene; and it was only after the application to this substance of the zinc dust method, discovered by Ad. Baeyer,* that Graebe and Liebermann succeeded in recognising Alizarine as a derivative of anthracene. The (to them) still unknown fundamental quinone they termed anthraquinone, and at the same time looked on Alizarine as a dioxyanthraquinone, on the strength of its similarity with chloroxynaphthalic acid and the oxynaphthaquinones.

The immediate consequence of this identification was the artificial preparation of Alizarine, by the same workers, in 1868, by fusing bibromanthraquinone with potash.

This first intentional synthetic preparation of dye-stuffs belongs to the most illustrious attainments of modern chemistry, and is almost unparalleled in the extent of its chemico-technical consequences.

The endeavours of Graebe and Liebermann to prepare Alizarine from a sulpho acid of anthraquinone were frustrated by their failure to sulphonate the primary material. They employed merely the same temperatures as were then customary for the production of sulphonic acids, and it was only later that H. Caro succeeded, by heating anthraquinone and

* All oxyanthraquinones are reduced to anthracenes when distilled with zinc dust.

sulphuric acid to over 200° C., in obtaining a sulpho acid that gave Alizarine when fused with potash.

This latter method of preparing Alizarine was patented conjointly by Caro, Graebe and Liebermann, whilst almost simultaneously Perkin patented the same reaction in England.*

These workers then amalgamated to secure the common fructification of their epoch-making discovery. The result was the establishment of works for the production of Alizarine—to some extent independently of the inventors, on account of the insufficient protection then afforded by the patent laws. The great technical difficulties initially in the way of producing Alizarine on a manufacturing scale were soon overcome, and the process then became one of the most important, and for a long time also the most profitable, tasks of the colour maker.

In the year 1888 the daily production of Alizarine in Europe amounted to 65 tons of 10 per cent. paste. In consequence of the keen competition and the gradual perfecting of the methods of manufacture, the price of Alizarine fell considerably, *e.g.*, from 6s. or 7s. per lb. in 1870 (for 10 per cent. paste) to about 10d. per lb. (for 20 per cent. paste) in 1900. At the present time the manufacture of Alizarine is only pursued by four makers in Germany, and by one firm (The British Alizarine Co.) in England, though it was also practised for a time in Russia, France, Switzerland and Austria.

This highly important branch of dye-stuff manufacture seems to have now reached its culminating point. For many purposes it is being found that Alizarine is not indispensable; and its consumption has been reduced by the employment of sundry azo dye-stuffs, such as p. Nitraniline Red.

* Caro, Graebe and Liebermann's English application was filed on 28th June, 1869, that of Perkin *one day later*!

The raw material employed is crude Anthracene from coal tar. This (30-40 per cent.) product is first purified by treatment with solvent naphtha, pyridine or acetone, which merely dissolve the impurities, the small portion of anthracene passing into solution being deposited again on cooling. The purified product contains about 50-55 per cent. of anthracene (or 80-90 per cent. when pyridine or acetone has been used),* the remainder consisting of other hydrocarbons, such as phenanthrene, fluorene, pyrene, etc.,† all of which are unsuitable for the production of colouring matters. To eliminate these, the impure anthracene is treated with potassium bichromate and sulphuric acid, which oxidise the anthracene and leaves the other hydrocarbons either unaltered or only partly oxidised. On then treating the mixture with moderately concentrated sulphuric acid (sp. gr. 1·84) at 105-110° C., the anthraquinone is dissolved without alteration, whilst the other hydrocarbons are converted into sulpho acids. The whole being poured into water, the sulpho acids alone are dissolved, and the anthracene is deposited. The purification is completed by a process of sublimation with superheated steam.

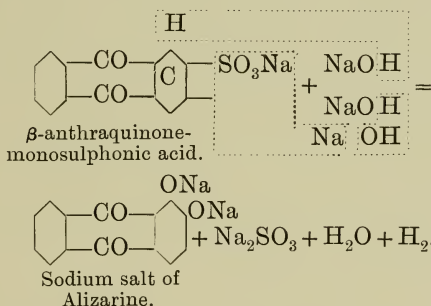
The resulting anthraquinone, which must be nearly chemically pure, is next sulphonated. In the early days of the Alizarine industry it was believed that Alizarine was formed from a disulphonic acid of anthraquinone; and it was not until later that the discovery was made that only the β -monosulphonic acid is suitable for this purpose, whereas the disulphonic acids furnish trioxyanthraquinone. A great progressive step was the introduction of fuming sulphuric acid (Koch), which enabled the mono- or the disulphonic

* The percentage of anthracene is determined by the Luck method: *Berl. Ber.*, 6, 1347.

† Basic substances: carbazol, acridine, etc., are also present in crude anthracene.

acid to be produced as required. If the sulphonation be effected at 150° C. with a sulphuric acid containing 15 per cent. of anhydride, the β -monosulphonic acid of anthraquinone is almost exclusively obtained; the process does not, however, go on in an entirely quantitative manner, a small portion of the anthraquinone being always left unaltered. The separation is effected by the sodium salt* of the sulphonic acid, which is distinguished from insoluble anthraquinone by being readily soluble in hot water.

To convert the first-named into Alizarine, it is fused with caustic soda for 2-3 days at 200° C., whereby the sulpho group is displaced by a hydroxyl, a second entering into the same nucleus at the same time:—



The caustic soda, therefore, also exerts an oxidising action, and the liberated hydrogen can reduce a portion of the Alizarine to monoxanthraquinone, or even to anthraquinone. This actually used to occur in the early days of the process, but is now obviated by adding sodium chlorate, or nitre, to the melt (Koch).

When the fusion process is completed, the mass is dissolved in water, and the Alizarine is recovered, in the form of leather-yellow flakes, by acidifying the violet coloured alkaline solution with hydrochloric acid. The product is

* This salt is known in practice as "silver salt," because formerly, when impure anthraquinone was used, it deposited in scales of silvery lustre.

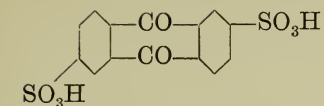
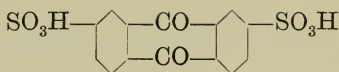
finally washed, and stirred up with water to form a paste containing a known quantity of dry matter. Formerly, 10 per cent. pastes, containing 10 parts of Alizarine to 90 parts of water, were produced; but at present the paste is almost exclusively of 20 per cent. strength. Some 40 per cent. pastes are, indeed, sold, but are attended with the disadvantage that, when they have stood for some time, they become so dry as to be difficult to restore to a homogeneous condition.

Large batches of Alizarine are made up at a time into 20 per cent. paste. In order to get regular results, and not overshoot the mark, it is usual to add the water by degrees, so as to obtain, in succession, 25, 22, 20·7 . . . 20 per cent. of dry substance. The work must, of course, be carefully checked continuously. If the paste has inadvertently been made too thin, it must be brought to the proper concentration by adding the requisite quantity of stronger paste.

The reason for selling Alizarine in the paste form is that, when once dry, it cannot again be distributed so uniformly and finely in water as is indispensably necessary to its employment in dyeing and printing.

For shipment to India, Alizarine is also prepared in the form of powder by drying the paste through an admixture of starch. When placed in water, the starch swells up, and the powder is converted into a thin pap suitable for the purposes of the dyer. At the present time most of the Russian dyers purchase their Alizarine in the form of powder, effecting the solution in soda and precipitation with hydrochloric acid in the dye-bath itself, this method giving more powerful dyeings than are obtainable with Alizarine paste.

If the sulphonation of anthraquinone be performed by heating it with an excess of sulphuric acid (with 40 per cent. of anhydride) at 280-350° C., there result two disulphonic acids, which are distinguished as *a* and *β*-acid:—

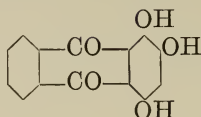
 α -anthraquinonedisulphonic acid. β -anthraquinonedisulphonic acid.

On fusing the sodium salts of these acids with caustic soda in presence of sodium chlorate, there are formed two trioxyanthraquinones : Flavopurpurine and Iso- or Anthrapurpurine. Both are produced in a perfectly pure state on the large scale, and, when mixed with Alizarine, serve for obtaining numerous marks of Alizarine dye-stuffs.

The product known in commerce as Alizarine with blue tinge is generally pure Alizarine (*e.g.*, the mark VI. of the B. A. S. F. ; mark I. extra of the Farbenfabriken, form. Fr. Bayer & Co., etc.), whereas the other marks of more yellowish tinge are mostly variable mixtures of Alizarine, Flavopurpurine, and Anthrapurpurine, or contain only one of these two latter.

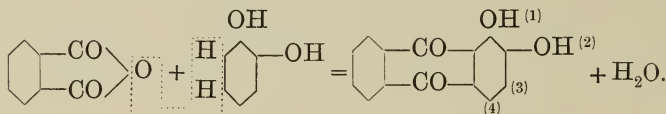
Whereas Alizarine is more used for the production of rose-red, violet, and Old Red (Turkey red by the old process), Flavopurpurine is particularly suitable for printing on cotton goods, since it combines with mordants more readily than the other two, and is developed by a merely gentle steaming. Finally, the more bluish Anthrapurpurine, and the Alizarine marks of which it is the chief constituent, are more used for dyeing, the alumina lake presenting greater resistance to soap baths.

A third trioxyanthraquinone, Purpurine, accompanies Alizarine in madder root, and is prepared synthetically by heating dry Alizarine to 100° C., with sulphuric acid, and oxidising with manganese peroxide (de Lalande); or by warming α -nitroalizarine (see below) with sulphuric acid (Caro); or, finally, by heating anthraquinone with concentrated sulphuric acid and boric acid. In composition it corresponds to the following formula :—



The position of the hydroxyl groups in Purpurine and in Alizarine was determined in the following manner:—

When phthalic anhydride and pyrocatechin are condensed by heating with an excess of concentrated sulphuric acid, Alizarine is formed:—



Phthalic anhydride. Pyrocatechin. Alizarine.

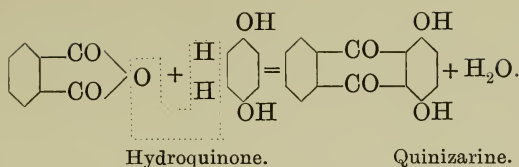
Syntheses of this kind have recently been made by Lagodzinski, *e.g.*, by heating dimethylhydroquinone with phthalic anhydride and aluminium chloride dissolved in carbon disulphide. This produces



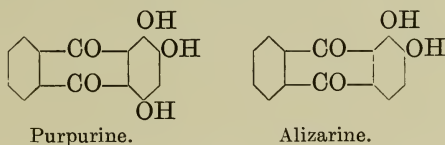
a derivative of benzoylbenzoic acid, which, on being heated with concentrated sulphuric acid, is converted into the corresponding derivative of anthraquinone.

From this synthesis it follows that the two hydroxyl groups in Alizarine must be in the ortho position to each other. Nevertheless, the condensation might have proceeded in such a manner that the hydroxyl groups would be in the position 2. 3. instead of 1. 2. (as in the above formula).

In a similar manner there has been obtained from hydroquinone a dioxyanthraquinone, which, owing to the method of formation, certainly contains the hydroxyl groups in the para position: the so-called Quinizarine.



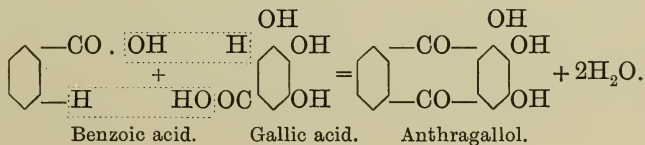
Now, since Purpurine is formed by oxidation, both from Quinizarine and Alizarine, it must, therefore, contain all three hydroxyls in one nucleus, and that, too, in the position 1. 2. 4. Consequently, the hydroxyls in Alizarine must be in the position 1. 2. and not 2. 3. :—



The Alizarine dye-stuffs hitherto considered, Alizarine, Flavopurpurine, Anthrapurpurine, and Purpurine, as also the Alizarine Orange to be described later on, exhibit very similar properties, both as dye-stuffs and in other respects. Their tin lakes are orange in colour, the alumina lakes orange to red, the chrome lakes Bordeaux, and the iron lakes violet. Purpurine, however, on account of its higher price and inferior fastness, is far less important than the rest.

All the other Alizarine dye-stuffs described below are not so decidedly polygenetic, and are almost entirely used only in the form of colour lakes in dyeing and printing, though to some extent also as acid dye-stuffs.

Anthragallol.—This dye-stuff is prepared by the Seubert method, *viz.*, by heating benzoic and gallic acid with concentrated sulphuric acid, a process which, at the same time, indicates its constitution:—



It can also be obtained by the condensation of phthalic acid and pyrogallol with sulphuric acid, analogous to the synthesis of Alizarine from phthalic acid and pyrocatechin.

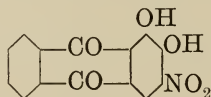
For a long time this dye-stuff remained unnoticed ; in fact, until, on the introduction of chrome mordant into the dyeing industry, its good qualities gained recognition. At present it is sold in the form of 20 per cent. paste, under the names Anthracene Brown and Alizarine Brown, and, thanks to its great fastness, is one of the most highly prized dyes for wool. Of late it has also been applied to silk and cotton ; only its chrome lake is of any practical value.

In a similar manner, by the condensation of gallic acid and cinnamic acid, a dye-stuff has been prepared, which has received the name of Styrogallol, but is not in practical use.

Alizarine S, WS, Alizarine Red in powder, etc. These are the commercial names applied to the sodium salts of Alizarine monosulphonate, and sulphonates of Flavo- and Anthrapurpurine. The corresponding acids are prepared by the action of strong sulphuric acid on Alizarine and the trioxyanthraquinones in question.

These sulphonated Alizarines serve for dyeing wool, a purpose for which Alizarine itself is not well adapted. They are sold in the form of powder.

Alizarine Orange.—This dye-stuff, which behaves in an entirely analogous manner to Alizarine, is produced by the action of nitric acid on Alizarine dissolved in nitrobenzol. It is a β -mononitroalizarine, corresponding to the formula :—



The nitro group enters the molecule of Alizarine with great facility, and that, too, at ordinary temperature, by the influence of nitrous fumes on Alizarine, or on a fabric dyed therewith. This last method of forming Nitroalizarine also

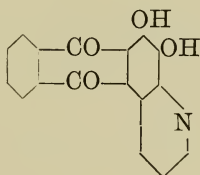
led to its discovery by Strobel. It has been scientifically investigated by Rosenstiehl.

Its chief use is in calico printing, though not on a very large scale. On reduction, it furnishes Amidoalizarine, which has been put on the market under the name Alizarine Chestnut (B. A. S. F.), but is of small practical importance.

The principal employment of these two last-named dye-stuffs is in the production of Alizarine Blue.

Alizarine Garnet R (M. L. Br.) is an α -amidoalizarine, obtained by nitrating benzoylalizarine, and reducing the product. Identical with this is Alizarine Cardinal (F. Bayer), prepared therefrom by nitrating the arsenic ether of Alizarine; whereas, strangely enough, the boric ether of Alizarine furnishes Alizarine Orange. These dye-stuffs are used, to a small extent, in calico printing.

Alizarine Blue.—This important dye-stuff was first discovered by Prudhomme, who prepared it by heating nitroalizarine (Alizarine Orange) with glycerine and sulphuric acid. Graebe, who subjected Alizarine Blue to scientific investigation, found that it should be regarded as an anthraquinoline corresponding to the formula:—



This assumption, that a quinoline compound is formed during this reaction, was very soon beautifully confirmed by Skraup's synthesis of quinoline by heating nitrobenzol and Aniline with glycerine and sulphuric acid. Skraup was induced to employ Aniline in this synthesis by the opinion, expressed by Graebe, that the poor yield was attributable to the oxygen liberated from the nitro group of the nitrobenzol.

The method now adopted for producing Alizarine Blue is similar to the synthesis of quinoline, *viz.*, by heating nitro- and amidoalizarine with glycerine and sulphuric acid to 105° C. On pouring the mass into water the Alizarine Blue is deposited, and is then washed to separate it from the pertinaciously adherent sulphuric. The yield of dye-stuff is almost quantitative.

Alizarine Blue S is the commercial name for the sodium bisulphite compound. It has the advantage of being soluble in water; and is chiefly used in calico printing. Another soluble sodium salt of Alizarine Blue is sold as Alizarine Blue XA (B. A. S. F.) and Alizarine Blue WA (Fr. By.), and is principally employed in wool dyeing.

Brilliant Alizarine Blue (Fr. By.) is a thiazine, and not an Alizarine dye-stuff at all.

By the action of formaldehyde, Prudhomme prepared from Alizarine Blue certain new dye-stuffs, which, however, have not yet attained any technical importance.

Alizarine Green S (M. L. Br.) is the quinoline derivative of Alizarine Garnet (α -amidoalizarine) corresponding to Alizarine Blue S, and in contrast to the isomeric Alizarine Blue furnishes green lakes.

Alizarine Black (M. L. Br.) is a β -quinoline of Flavopurpurine.

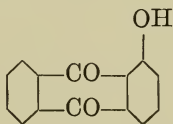
With the exception of Alizarine Green, Alizarine Chestnut, and Alizarine Garnet, all the Alizarine dye-stuffs hitherto described belong to the older members of this group. For a long time it seemed as though no further technical advance was possible in this branch; but in 1888 R. Bohn (B. A. S. F.) discovered a reaction, the full importance of which was first recognised by R. E. Schmidt (Fr. By. & Co.), and which forms the by no means exhausted source of a number of valuable new dye-stuffs. This reaction consists in the

introduction of hydroxyl groups, through the oxidising action exercised by a high-percentage fuming sulphuric acid at moderate temperature. The first products are anhydrides of sulphonic acids (ethers), which, when treated with acids, furnish free polyoxyanthraquinones. These latter have been scientifically studied by Graebe, and by Schmidt and Gattermann.*

Bohn first applied the reaction to Alizarine Blue, and R. Schmidt then used it with Alizarine. It was, however, soon found that it could also be used with all the anthraquinone derivatives as well as with anthraquinone itself. A further important advance made by R. Schmidt was the conjoint employment of boric acid, which forms ethers with the oxyanthraquinones, and thus protects them from further oxidation.

This method has not only led to the production of a series of new and technically valuable dye-stuffs, but also to an improved process of manufacturing the already known oxyanthraquinones.

Thus anthraquinone, on being heated with concentrated sulphuric acid and boric acid, readily furnishes Quinizarine, and, on further exposure, Purpurine; erythroxyanthraquinone,

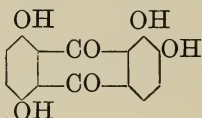


is at once converted into Anthrarufine by sulphuric acid, rich in anhydride, and into hexaoxyanthraquinone on prolonging the reaction. Other oxidising agents, such as persulphate, perchloric acid dissolved in concentrated sulphuric

* Graebe, *Berl. Ber.*, 1890, 3739 b; Graebe and A. Philips, *ibid.*, 1891, 2297 b; *Ann. Chem.*, **276**, pp. 21-35. See also R. Schmidt and Gattermann, *Journ. f. prakt. Chem.*, **44**, pp. 103-109.

acid, electrolytic oxygen, etc., have also been patented for the same purpose.

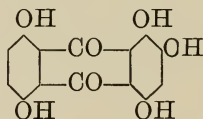
Alizarine Bordeaux (By.).—This dye-stuff is prepared by heating dry Alizarine for 3-4 days at 30-40° C. with sulphuric acid containing 80 per cent. of anhydride. It is a dioxy-alizarine of the following constitution:—



The alumina lake of this dye-stuff is Bordeaux red in colour, the chrome lake a violet blue. In its purest form it is known as Alizarinecyanine 3R.

The oxidation of Alizarine Bordeaux with manganese peroxide and sulphuric acid furnishes

Alizarinecyanine R (By.),



a pentaoxyanthraquinone which gives a handsome blue chrome lake.

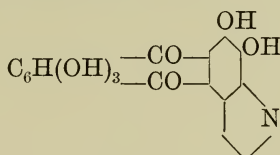
Alizarinecyanine G (By.).—This and similar dye-stuffs are produced by the action of ammonia on the intermediate products formed in the preparation of Alizarine Bordeaux; and are also prepared from Flavo- and Anthrapurpurine, instead of Alizarine. They give more greenish-blue dyeings than the R marks of Alizarinecyanine.

The mark 3G, a polyamidooxyanthraquinone sulphonic acid, can also be employed, as an acid dye-stuff, for dyeing wool, on which it gives dyeings more equally distributed and faster to light than other acid dye-stuffs.

Alizarine Green S, Alizarine Blue-green, and Alizarine Indigo Blue (B. A. S. F.) were the first dye-stuffs produced

by the Bohn method. They are prepared from Alizarine Blue instead of from Alizarine, and are, therefore, polyoxy-anthraquinolines.

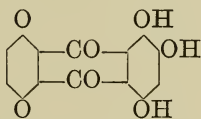
Alizarine Green mainly consists of a sulphonic acid of a monoxyalizarine blue, in addition to which it contains a small quantity of a dioxyalizarine blue. An isomeric sulpho acid of monoxyalizarine blue forms the main constituent of Alizarine Blue-green, whilst Alizarine Indigo Blue is chiefly composed of a trioxyalizarine blue :—



besides containing dioxyalizarine blue and a sulpho acid of the same.

For preparing such polyoxyanthraquinolines, Fr. Bayer & Co. propose a reversed plan, by converting polyoxyanthraquinones (*e.g.*, Alizarine Bordeaux) into the corresponding anthraquinoline derivatives by nitration and quinolation.

In the formation of all these polyoxyanthraquinones, peculiar intermediate products are obtained, especially when the oxidation is performed at very low temperature. These compounds are regarded as anthradiquinones, *e.g.* :—



Quinone of Alizarinecyanine R.

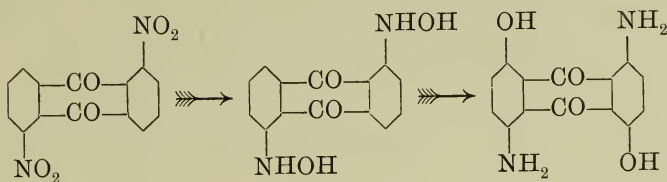
These are condensed to new dye-stuffs by phenols, without being first isolated. When treated with ammonia, mordant dye-stuffs of the quinonimide type are obtained.

Dye-stuffs from Dinitroanthraquinone.

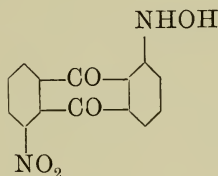
A further technically important advance was made by the application of the Bon-Schmidt reaction to nitrated anthraquinones. The first advantage consisted in the employment of dinitroanthraquinone (1. 5. and 1. 8.), a very cheap raw material. The earliest experiments in this direction were made ten years earlier by von Perger, but without leading to any technical result. At present the reaction is performed with or without addition of sulphur and boric acid, and its course is largely dependent on the working conditions. Thus, when dinitroanthraquinone, for example, is heated with fuming sulphuric acid and sulphur, without boric acid, the products are different from those obtained when this last-named acid is allowed to take part in the reaction. The best results are obtained at a low temperature, and in presence of sulphur. This latter—as sulphur sesquioxide, S_2O_3 —exerts a reducing action, and may also be replaced by other reducing agents. The resulting soluble products are converted, by heating with ordinary sulphuric acid, into the valuable insoluble dye-stuffs, all of which are blue mordant dye-stuffs. These are partly non-nitrogenous polyoxyanthraquinones; consequently, in their preparation, the nitro groups must have been eliminated, and replaced by hydroxyl groups. Until very recently the course of this very complex reaction was involved in obscurity; all that could be supposed was that a reduction of nitro groups to amido groups was in question, the latter being afterwards replaced by hydroxyl groups, under the influence of the sulphuric acid.

It has now been discovered by Gattermann and R. Schmidt that 1. 5. dinitroanthraquinone is converted, by slight reduction in alkaline solution, into the corresponding dihydroxylamine, which, under the action of sulphuric acid,

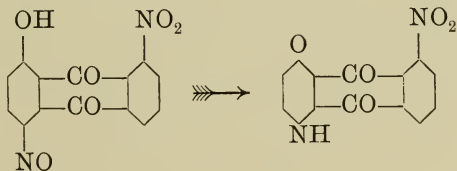
is transposed into different isomeric diamidodioxyanthraquinones :



By a very gentle process of reduction they also succeeded in showing the occurrence of a monohydroxylaminenitroanthraquinone :



Again, in the technically so important sulphur sesquioxide method, the first product formed from the dinitroanthraquinone—and that, too, even at ordinary temperature—is the hydroxylamine derivative. The course of the reaction is, however, partly different; it would appear that—analagous to what occurs in the formation of naphthazarine (see later)—migration of an oxygen atom of the nitro group in the nucleus results in the production of a nitronitrosooxyanthraquinone, which is probably converted, by reduction, into a quinonimide* :



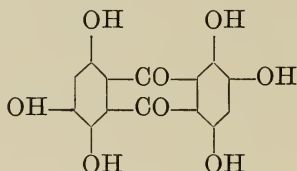
* The appearance of a quinonimide intermediate product has been proved direct by the action of fuming sulphuric acid on dinitroanthrachrysonedisulphonic acid, and also in other cases.

The finally resulting amido groups are converted into hydroxyls by the oxidising action of the sulphuric acid.*

A very important dye-stuff produced by this method is :—

Anthracene Blue (B.), which is very similar to Alizarine-cyanine.

The mark WR is a hexaoxyanthraquinone of the following composition :—



The marks WG and Anthracene Dark Blue† are also extensively used. An analogous product is the beautiful Brilliant Alizarinecyanine G and 3G (By.).

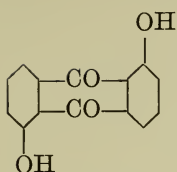
Another member of this series is Alizarinecyanine Black (By.), which is distinguished by special fastness to light.

Anthracene Blue Cyanine and Alizarinecyanine, which are partly identical, are superior to the older Alizarine Blue in equalising power and penetration, besides possessing greater tinctorial power, and being, therefore, more economical. On the other hand, Alizarine Blue excels them in fastness to milling.

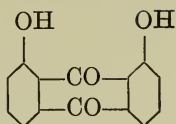
Certain new blue dye-stuffs, of good equalising power, capable of dyeing wool in an acid bath, and of being fixed with mordants, are prepared by Fr. Bayer & Co. from Anthrarufine and Chrysazine :

* A similar displacement of NH_2 by OH can also be effected by other oxidising agents.

† Is a waste product in the preparation of Anthracene Blue, and consequently very cheap.

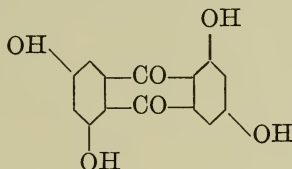


Anthrarufine.



Chrysazine.

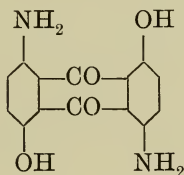
and by M. L. Br. from Anthrachryson* :



by successive sulphonation, nitration and reduction. For the most part the amido groups are finally replaced by hydroxyl groups.†

The most important member of this series is

Alizarinesaphirol (By.), a disulphonic acid of diamido-anthrarufine :

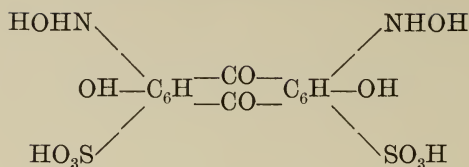


The discovery of this dye-stuff (by R. Schmidt) may be regarded as the most important progressive step made of late in the group of the Alizarine dye-stuffs, this product meeting the requirements of the wool dyer for a blue dye-stuff, fast to light, and of good equalising power.

Theoretically interesting, on account of their great stability, are the dihydroxylamine compounds :—

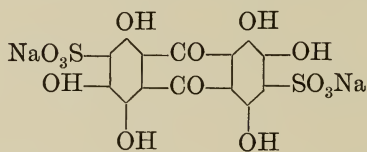
* Produced from sym. dioxybenzoic acid and fuming sulphuric acid.

† Anthraflavine and i. anthraflavine (1. 6. or 1. 7. dioxyanthraquinone) are also converted into dye-stuffs in the same way.



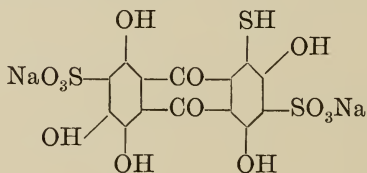
obtained from dinitroanthrarufine (-chrysazine) disulphonic acid, by incomplete reduction. They are distinguished by their capacity for crystallising, and they dye both mordanted and unmordanted wool blue.

Alizarine Acid Blues (M. L. Br.) are prepared from Anthrachrysone, and consist of polyoxyanthraquinone disulphonic acids. The mark BB is a hexaoxyanthraquinose disulphonic acid, to which the following constitution is ascribed :—



These dye-stuffs are applied to wool in an acid bath, without, however, producing a useful colour; and, when fixed with chrome, a complete change of colour results.

Alizarine Acid Green (M. L. Br.), which is prepared by reducing dinitroanthrachrysone disulphonic acid with sodium sulphide, probably has the following formula :—



Finally, two other green Alizarine dye-stuffs are worthy of mention. The bright Alizarine Viridine, which is best adapted for printing, and Alizarinecyanine Green (both By.), which is extremely fast to light, and gives dyeings on chrome mordanted wool that are fast to milling. The latter gives a

direct green on wool, and no alteration of shade is produced by chroming (see later).

All these Alizarine dye-stuffs play a very important part in the production of fast blues and greens on wool. As already mentioned, only their chrome lakes are used in practice; the sole exceptions being Bayer's Alizarine Bordeaux and Alizarine Heliotrope, which are also used in the form of alumina lakes, for the production of amethyst shades in calico printing.

A number of new patents taken out by Bayer & Co. describe Alizarine dye-stuffs obtained by the condensation of different anthraquinone derivatives with aromatic amines and phenols. Polyoxyanthraquinones are condensed with primary aromatic bases, in presence of hygroscopic agents—whereby 2 molecules of the said bases are fixed—the products being then sulphonated. A dye-stuff prepared in this manner is Alizarine Blue-black B, another being Alizarine Heliotrope 3B (By.). The same reaction is given by dinitroanthrarufine (-chrysazine) sulphonic acids, which furnish greenish-blue dye-stuffs. The most valuable of the dye-stuffs, however, prepared by this process, seem to be those formed by the condensation of leucoquinizarine (a reduction product of quinizarine) with aniline, p. toluidine, etc., followed by oxidation and sulphonation. These are identical with those furnished by the condensation of quinizarine itself with amines. Alizarinecyanine green (By.) also belongs to the same series. In addition, polyoxyanthraquinone sulphonic acids—in the form of esters—are condensed with phenols, oxycarbo acids, etc., to dye-stuffs which dye wool in an acid bath.

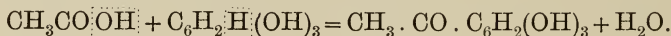
The action of aromatic amines on nitroanthraquinones furnishes anilido derivatives, the sulphonic acids of which form fast red and green acid dye-stuffs.

Of other technical novelties in this branch, mention may be made of the following: If sulphonic acids of alizarine dye-stuffs be treated, in dilute aqueous solution, with chlorine or bromine, the sulpho groups are replaced by halogens. The resulting dye-stuffs behave, in general, like those from which they have been produced, though they are claimed to have greater fastness to milling.

II. OXYKETONE DYE-STUFFS OF DIVERGENT CONSTITUTION.

To these belong a number of dye-stuffs, which in practice are classed along with the Alizarine dye-stuffs, in consequence of their mode of application and their fastness. They are all mordant dye-stuffs, some being "dyes," others "dye-stuffs". Only the chrome lakes are in practical use.

Alizarine Yellow (B. A. S. F.).—The different marks of this dye-stuff result from the condensation of pyrogallol with various acids, such as acetic acid, benzoic acid, salicylic acid, etc. Thus the mark C, which is also known as gallacetophenone, is obtained by the action of glacial acetic acid on pyrogallol in presence of zinc chloride:—



Acetic acid.

Pyrogallol.

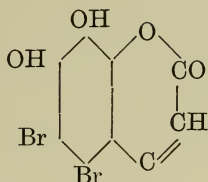
Alizarine Yellow C.

These dye-stuffs are somewhat fugitive to light.

The mark A is prepared by the condensation of pyrogallol and benzoic acid (or benzo trichloride in presence of 90 per cent. alcohol), its composition, therefore, corresponding to the formula $\text{C}_6\text{H}_5 - \text{CO} - \text{C}_6\text{H}_2(\text{OH})_3$.

Similar yellow mordant dye-stuffs have been prepared by Noelting and A. Meyer, by the condensation of resorcine, pyrocatechin, and pyrogallol, with pyrocatechuic acid and gallic acid.

Anthracene Yellow (By.) is a dye-stuff of the following composition :—

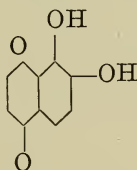


obtained by treating dioxy β -methylcumarine with bromine.

The Alizarine Yellow of the Hoechst Farbwerke is an azo dye-stuff that has already been described.

Alizarine Black S (B. A. S. F.).—This valuable dye-stuff for wool is the sodium bisulphite compound of naphthazarine, a dioxynaphthoquinone. Naphthazarine was known as long ago as 1861 (Roussin); but, as was the case with anthragallol, its valuable dyeing properties were long ignored; * and it was only in 1886 that Bohn made the important discovery that naphthazarine can be converted by sodium bisulphite into a soluble compound that will furnish a handsome fast black dyeing with chrome mordants. The chrome lake offers unusual resistance to the action of acids, and in this respect Alizarine Black is unequalled by any other black dye-stuff.

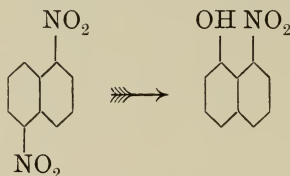
It can be prepared from either 1. 5. or 1. 8. dinitro- and also from 1. 4. 7. 8. tetranitronaphthalene, and is, therefore, regarded as 1. 2. dioxy-*a*-naphthoquinone,



At the present time it is obtained by treating crude

* That naphthazarine is a dye-stuff was known, and Roussin described its various lakes, except the chrome lake.

dinitronaphthalene (a mixture of 1. 5. and 1. 8. dinitronaphthalene) with fuming sulphuric acid and sulphur. According to Gassmann, however, it may be advantageously prepared by heating 1. 5. dinitronaphthalene with fuming sulphuric acid and infusorial earth. The progress of the reaction has been determined by Friedlaender and Scherzer,* who found that, by the migration of oxygen from one of the nitro groups, there is formed an intermediate product, nitro-nitrosonaphthol :



which can be reduced to a quinonimide, that in turn is readily hydrolysed to naphthazarine. This latter can be condensed, both with amines and phenols, to form new dye-stuffs, *e.g.* :—

Alizarine Black SRA (B.), the bisulphite compound of the condensation product of naphthazarine and aniline.

Alizarine Dark Green (B.), formed by the condensation of naphthazarine with phenol.

I. naphthazarine, a body of similar composition, which is obtained by oxidising β -naphthoquinone with hypochlorous acid, gives dyeings that are fugitive to light, and is, therefore, of no practical value.

An Oxynaphthazarine (Naphthopurpurine) furnishes red dyeings on alumina mordants.

The following dye-stuffs may also be included in this group :—

Carmic acid, the tinctorial principle of cochineal. The constitution has not yet been elucidated, notwithstanding numerous researches in this connection. W. v. Miller and

* *Mitth. des k. k. Technol. Gew.-Museums.* Vienna, 1900, pp. 11-32.

G. Rohde believed it should be regarded as a naphthoquinone derivative; but the accuracy of this view appears questionable in the light of more recent investigations.

Carmic acid occupies an intermediate position between "dyes" and "dye-stuffs," possessing, as it does, fairly considerable tinctorial power, though the dyeings thereby produced are not utilised in practice. Its tin lake (Cochineal Scarlet) and alumina lake are important.

Galloflavine (B. A. S. F.).—The dye-stuff sold under this name probably belongs to the oxyketones; but its composition has not yet been investigated. It is prepared by exposing a faintly alkaline solution of gallic acid to prolonged oxidation by atmospheric oxygen.

The greenish-yellow chrome lake of Galloflavine is occasionally used in wool dyeing, either alone or combined with Alizarine dye-stuffs, to replace Fustic. The dyeings, however, are rather fugitive to light.

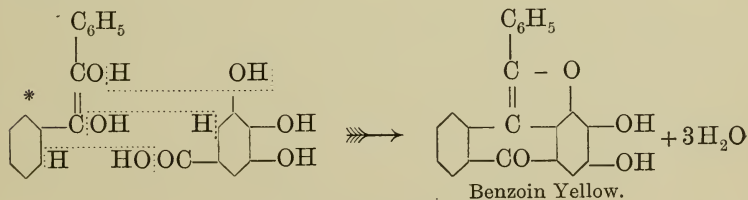
Reso flavine (B.) is a new dye-stuff prepared by oxidising sym. dioxybenzoic acid.

Yellow mordant dye-stuffs (B.) have also been prepared from salicylic acid, by oxidation with persulphate and with electrolytic oxygen.

Benzoin Yellow (B.) is a fugitive yellow mordant dye-stuff, obtained by the condensation of benzoin,

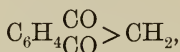


with gallic acid (and sulphuric acid). Graebe expresses the origin and constitution of this product in the following manner:—

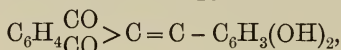


* Tautomeric form of benzoin.

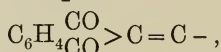
Benzalindandiones and benzalindanones have been prepared by Kostanecki. Indandione,



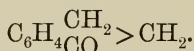
furnishes, by condensation with pyrocatechuic aldehyde,



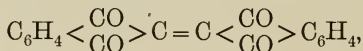
a dye-stuff which colours alumina mordants yellowish-red. Substances of analogous composition to this, and, therefore, containing the atomic complex,



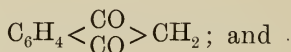
are termed by Kostanecki Carbindogenides. Weaker dye-stuffs are prepared in a similar manner from Indanone,



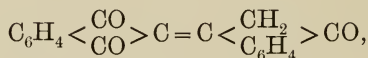
To the Carbindogenides also belong Indenigo,



obtained by Kaufmann from the oxidation of diketohydrindene,

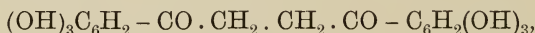


Bindone,



prepared by W. Wislicenus and A. Koetzle by boiling diketohydrindene with water.

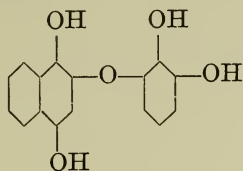
A Digallacyl,



was obtained by the author from the condensation of succinic anhydride with pyrogallol (by zinc chloride). This compound is quite white, and imparts a yellow colour to alumina mordants.

Friedlaender and S. Blumenfeld prepared new dye-stuffs by condensing naphthoquinones with phenols; the dye-

stuff produced from α -naphthoquinone and pyrogallol has the following constitution:—

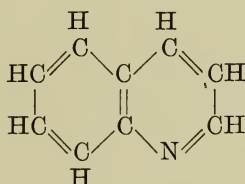


Compounds of analogous constitution have been prepared by A. Fischer and Schaar-Rosenberg from naphthoquinones and amines.*

QUINOLINE AND ACRIDINE DYE-STUFFS.

A. QUINOLINE DYE-STUFFS.

Quinoline is a base, consisting of a benzol nucleus and a pyridine ring,

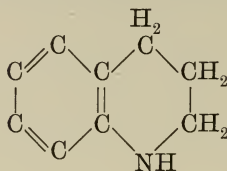


and is prepared, by the Skraup method, by heating nitrobenzol, aniline, glycerine, and sulphuric acid (see Intermediate Products, p. 35, and Alizarine Blue, p. 239).

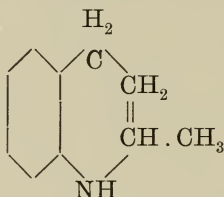
Up to the present it has been seldom used in the synthesis of dye-stuffs, not being so suitable for that purpose as the aromatic amines. It is only when hydrated in the pyridine ring that it acquires the faculty of furnishing dye-stuffs, through certain typical reactions, analogous to the aromatic amines. In such event it behaves like an aniline, alkylated

* *Berl. Ber.*, 1899, 83.

on the nitrogen.* Thus tetrahydroquinoline, for instance,



reacts with diazo compounds to furnish p. azo dye-stuffs; and violet to green dye-stuffs of the triphenylmethane series have been obtained from tetrahydroquinoline: †

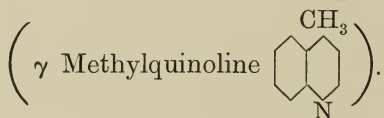


The tetrahydronaphthoquinolines also behave analogous to the naphthylamines.

So far as experience extends, it would appear that quinoline is not a suitable material for the production of dye-stuffs; and of the quinoline dye-stuffs hitherto prepared, only a single one, Quinoline Yellow, has any real practical value.

The tinctorial properties, which have a certain theoretical interest, of the oxyquinolines and their oximes, have already been mentioned.

Cyanine (Williams, 1861) is one of the oldest artificial dye-stuffs. It is prepared by the action of caustic alkalis on the product of the reaction of amyl iodide on a mixture, in equal molecular proportions, of quinoline and lepidine:—



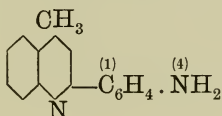
* *Ann. Chem.*, **257**, pp. 21, 28.

† *Berl. Ber.*, **24**, 1715.

This dye-stuff is as fugitive as it is handsome, and is used in the preparation of orthochromatic plates for photographic purposes, but not in dyeing.

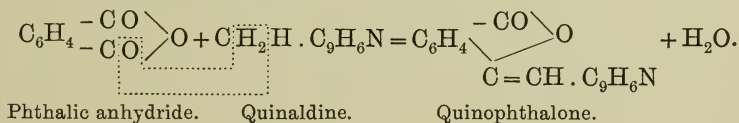
Quinoline Red.—This also handsome and fugitive dye-stuff exhibits a beautiful fluorescence, and is used in the same way as Cyanine. It is prepared by the action of benzol trichloride on a mixture of quinaldine and isoquinoline, in presence of zinc chloride (Jacobson, 1882), and probably, therefore, belongs to the group of triphenylmethane dye-stuffs.

Flavaniline.—Heating acetylated bases with zinc chloride furnishes dye-stuffs (M. L. Br. extinct patent), of which Flavaniline is worthy of note. It is prepared by heating acetanilide with zinc chloride to 250-270° C., and is an *α*-amidophenyllepidine, corresponding to the formula:—



Its sulphonic acid (Flavaniline S) produces noteworthy handsome yellow dyeings, of greenish tinge, on animal fibres; but, like Flavaniline itself, this dye-stuff is no longer made.

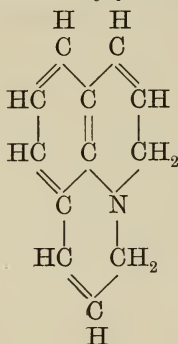
Quinoline Yellow S.—If quinaldine be allowed to react on phthalic anhydride, in presence of zinc chloride, there is formed a yellow dye-stuff, of the phthaleine type of constitution, *viz.*, Quinophthalone:



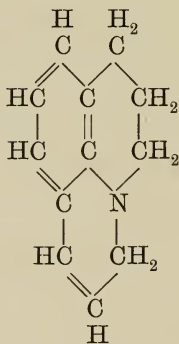
Quinophthalone is a technically valueless soluble dye-stuff; but when heated with fuming sulphuric acid, is converted into a disulphonic acid, the sodium salt of which, under the

name of "Quinoline Yellow," plays a great part in the dyeing of silk and wool. It is an acid dye-stuff of a somewhat high degree of fastness, and is particularly distinguished for the pure, greenish-yellow shade of its dyeings.

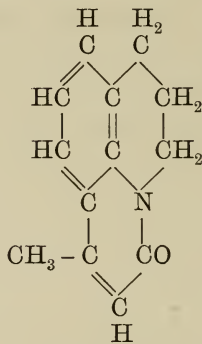
For the sake of completeness, mention must here be made of certain dye-stuffs of this group, which for the present have only a theoretical interest. The action of acetic ester on tetrahydroquinoline furnishes a substance, which is derived from a hypothetical body ("Julol") and is described as a ketomethyljuloline:



Julol.

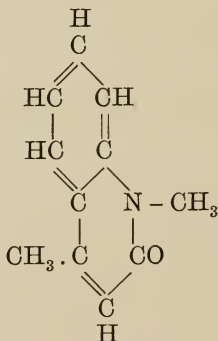


Juloline.



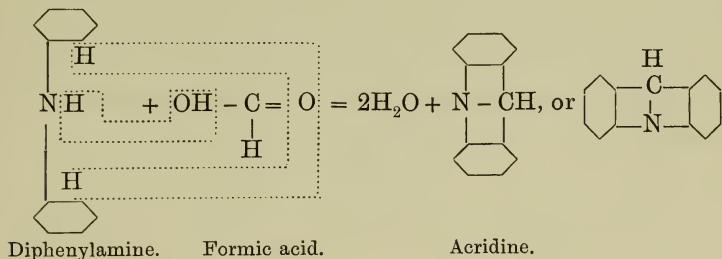
Ketomethyljuloline.

On allowing phosphorus pentachloride (and a little oxychloride) to react on ketomethyljuloline, a dye-stuff known as "Julol Violet" is obtained. Under corresponding circumstances, methyllipidone furnishes the very similar Lepidone Violet:



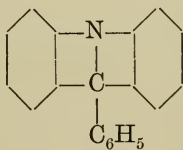
B. ACRIDINE DYE-STUFFS.

The fundamental substance of this group of dye-stuffs is acridine, a body present in coal tar and also prepared synthetically from diphenylamine and formic acid:



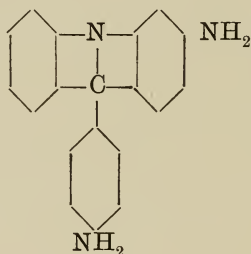
Acridine, however, cannot be used as the raw material for the production of the dye-stuffs derived therefrom, and is, therefore, of itself, without any practical value.

As already mentioned in connection with the triphenylmethane dye-stuffs, there invariably forms, in the fuchsine melt, *inter alia*, a yellow dye-stuff: the Chrysaniline discovered by Hofmann. This was isolated by Nicholson, who introduced its nitric acid salt into commerce under the name of Phosphine. As the first yellow basic dye-stuff, this played an important part at one time; but its position has now been seriously jeopardised by several other synthetic dye-stuffs, such as Rheonine (B.), Coriphosphine (By.), and Patent Phosphine (Ges. f. chem. Ind.). It is largely used in the dyeing of leather, and also in calico printing. In 1884 the constitution of Chrysaniline was determined by O. Fischer and Koerner, who, from its tetrazo compound, obtained the already known phenyl-acridine:

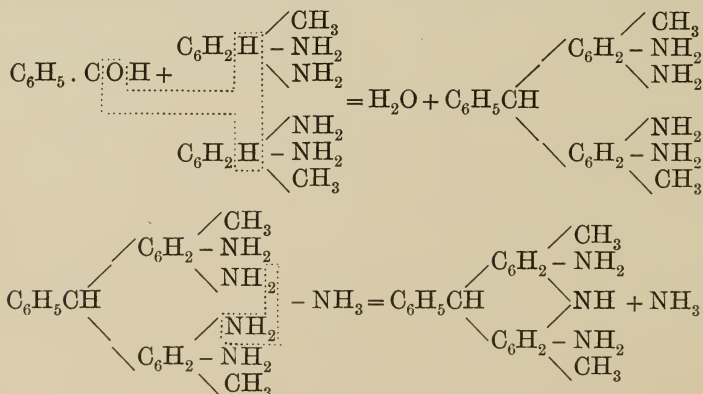


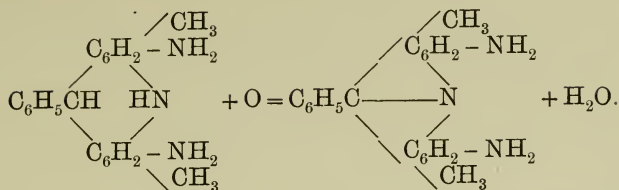
Consequently, Chrysaniline is a diamidophenylacridine. Shortly afterwards, its synthetic preparation from aniline and o. nitrobenzaldehyde at once explained its formation in the fuchsine process as the result of a concurrent "orthocondensation" (see p. 154), and revealed the para position of the amido groups towards the carbon attached to the three benzol nuclei.

Chrysaniline, therefore, has the following constitutional formula :—

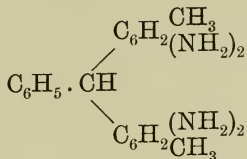


Further advance was made by the production of Benzo-flavine—homologous and isomeric with Chrysaniline—by Oehler in 1882, by the condensation of benzaldehyde and metatoluylenediamine. In this case the acridine ring is formed by elimination of ammonia, the resulting hydroacridine being converted into dye-stuff by oxidation. This synthesis can be represented by the following equations :—

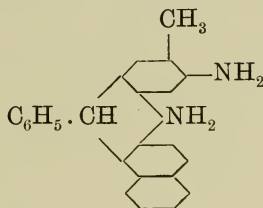




On heating the foregoing intermediate product, of the formula



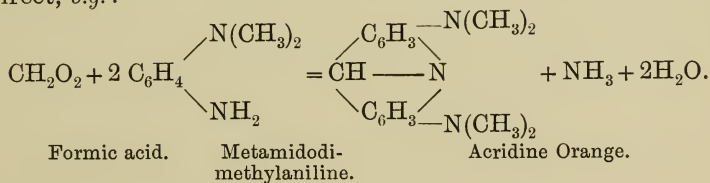
with β -naphthol, elimination of 1 molecule of m. toluylene-diamine (T. Ullmann) occurs, and the leuco base of a naphthacridine :



is formed.

In this process, benzaldehyde was afterwards replaced by its nitrated and amidised derivative, and finally by formaldehyde; *i.e.*, the same method that led to the New Fuchsine process in the group of the triphenylmethane dye-stuffs (*q.v.*).

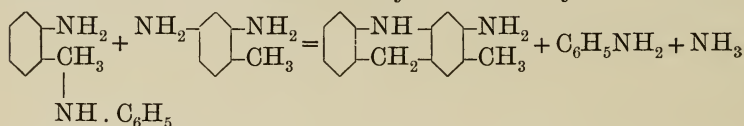
By the condensation of formaldehyde, or formic acid, with metatoluylenediamine, A. Leonhardt obtained Acridine Yellow, and with metamidodimethylaniline the more important Acridine Orange. On heating the aforesaid components in presence of a condensing agent, the dye-stuff is formed direct, *e.g.* :—



As can be seen, this process bears a certain resemblance with that by which the Pyronines are formed (*q.v.*). The dye-stuffs Acridine Red and Acridine Scarlet (L.) are mixtures of Acridine Orange and Pyronine.

Of late, other methods of producing the Acridine dye-stuffs have been made known.

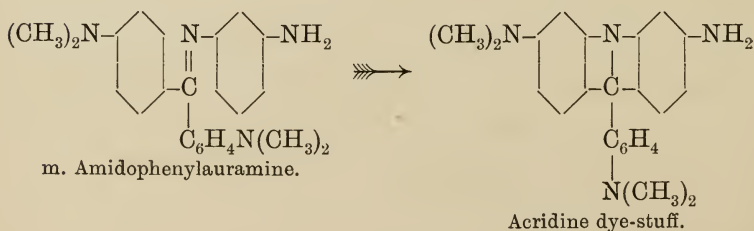
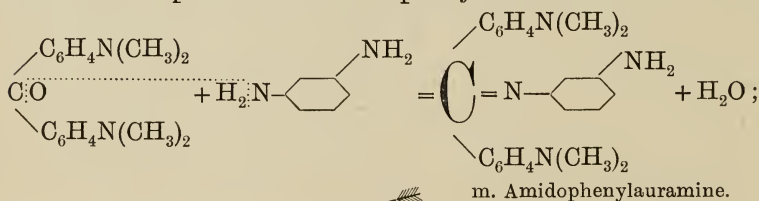
Whereas, in the above synthetic processes, it is necessary to take 2 molecules of the expensive metadiamine, Acridine dye-stuffs can now be prepared—according to patents of the Hoechst Farbwerke—from 1 molecule of this substance by condensation with *o.* amidobenzylaniline. Hydroacridines:



o. Amidobenzylaniline.

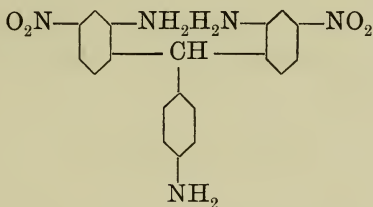
are first formed, which are oxidised into dye-stuffs by the action of atmospheric oxygen.

According to patents of the Badische Anilin- und Soda-fabrik, Acridine dye-stuffs can be produced by fusing tetralkylated diamidobenzophenone with *m.* phenylenediamine chloride and zinc chloride. As may be seen from the following equation, there is formed during this process the intermediate product *m.* amidophenylauramine:—



By this method are produced the Rheonines, dye-stuffs mainly used for dyeing leather.

Finally, the Hoechst Farbwerke have prepared various Chrysanilines by a reaction resembling the Fuchsine process, *viz.*, by oxidising p. toluidine and m. nitraniline with ferric chloride. The first products are evidently triphenylmethane derivatives:—



which are then converted into Acridine dye-stuffs by elimination of ammonia and by oxidation.

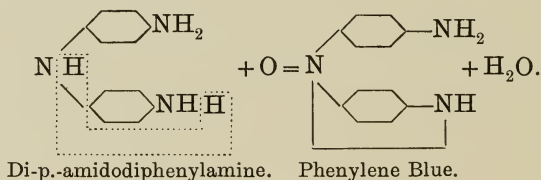
On treating the various amidoacridines with alkylating agents (dimethyl sulphate), the Ges. f. Chem. Industrie (Basle) prepares "Patent Phosphines". The Coriphosphines of Fr. Bayer & Co. also appear to be alkylated Amidoacridine dye-stuffs.

QUINONIMIDE OR DIPHENYLAMINE DYE-STUFFS.

INDAMINES, INDOPHENOLS, THIAZINES, OX-
AZINES, EURHODINES, SAFRANINES AND
INDULINES.

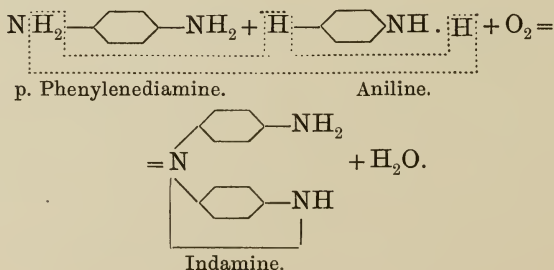
GENERAL REMARKS.

When di-p.-amidodiphenylamine is oxidised with potas-
sium bichromate, there is formed a blue dye-stuff, known as
Indamine or Phenylene Blue :

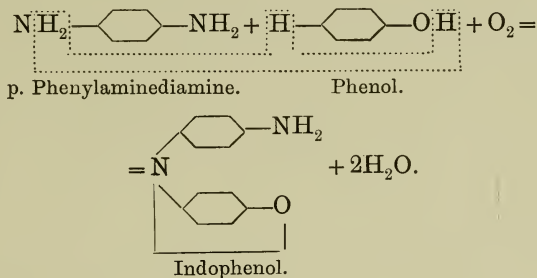


From this are derived a whole group of dye-stuffs, which
are, therefore, named "Indamines".

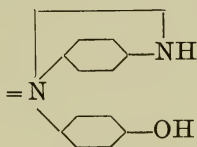
The above simplest form of Indamine is formed by the
oxidation of equal molecular proportions of p. phenylenedi-
amine and aniline with potassium bichromate in neutral
aqueous solution :—



If, however, p. phenylenediamine be oxidised with phenol, or p. amidophenol with aniline in an alkaline solution, the product is Indophenol, a hydroxyl derivative analogous to Indamine :



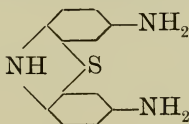
The formula of this substance is not



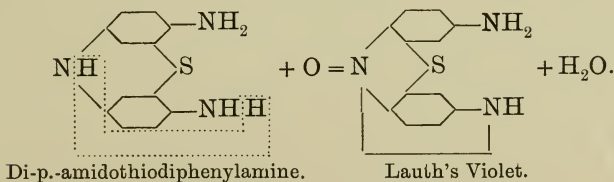
since it is a weak base, and does not behave like a phenol.

All substances constituted in the above manner are termed "Indophenols".

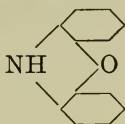
On oxidising di-p.-amidothiodiphenylamine,



a dye-stuff, also of analogous composition to Indamine Blue, is obtained. This, however, contains in addition an atom of sulphur uniting the two phenyl radicles :—



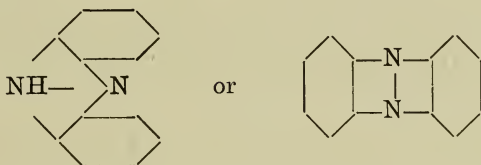
If the oxygen in Phenoxazine,



be pictured as replaced by an imide group, we then have Hydrophenazine,



from which are derived the Eurhodines, Safranines, and Indulines. Consequently they contain as their fundamental atomic group



the so-called Phenazine. The compounds belonging to this group are generalised under the name "Azines"; and the

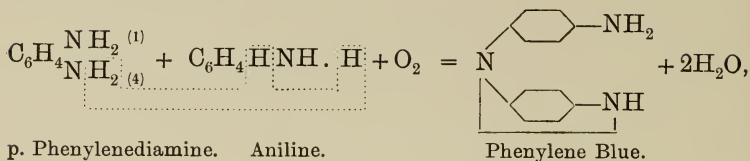
atomic complex $\begin{array}{c} -N- \\ | \\ -N- \end{array}$ is termed the Azine group.

The detailed constitution of these compounds will be gone into later on.

INDAMINES.

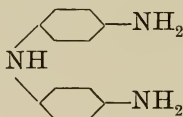
The formation of these dye-stuffs has really been long known, since they were produced by Runge and Perkin in the case of oxidation experiments with Aniline. They only became of interest, however, when found as intermediate products in the formation of Safranines (*q.v.*).

As already mentioned, the simplest dye-stuff of this group, Phenylene Blue,



is formed when p. phenylenediamine and aniline are oxidised, in neutral aqueous solution, with potassium bichromate.

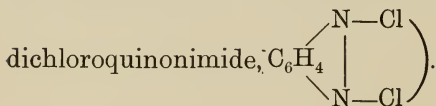
On reduction it is transformed into the leuco base



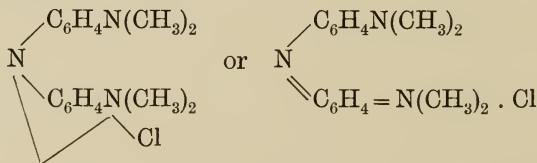
a substance identical with diamidodiphenylamine. Conversely, this latter compound furnishes Phenylene Blue on oxidation.

Indamines are also formed when p. phenylenediamine is replaced by other paradiamines, or aniline by other monamines with free para position, or by metadiamines.

In the above reaction, moreover, p. phenylenediamine can also be replaced by such substances as furnish paradiamines on reduction, *e.g.*, nitrosodimethylaniline, $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \text{ }^{(1)} \text{NO} \text{ }^{(4)}$ (or



Bindschedler's Green,



is furnished by the conjoint oxidation of dimethyl-p.-phenylenediamine and dimethylaniline.

Witt's Toluylene Blue, $\text{N} \begin{array}{l} \diagup \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \\ \diagdown \text{C}_6\text{H}_2 \begin{array}{l} \text{---NH}_2 \\ \text{---CH}_3 \\ \text{=NH} \end{array} \end{array}$, is produced in an

analogous manner from dimethyl-p-phenylenediamine and m. toluylenediamine. When heated in aqueous solution it is transformed into a Eurhodine, Toluylene Red.

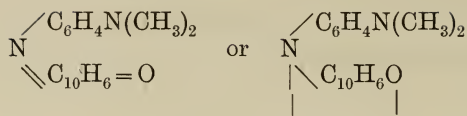
From p. phenylenediamine and m. toluylenediamine is obtained a simpler Toluylene Blue, which, in a similar manner, is transformed into a Eurhodine, "simplest Toluylene Red". This nomenclature originated in the circumstance that, at first, before the Eurhodines were known, it was customary to speak of "dye-stuffs of the Toluylene Red group".

All the Indamines are green to blue in colour. They are not used in dyeing, owing to their low power of resisting acids, which latter, when present in sufficient excess, decompose them into quinones and amines. They, however, possess a high theoretical interest as intermediate products in the preparation of Safranine (*q.v.*).

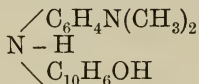
INDOPHENOLS (1881).

These dye-stuffs are formed by the oxidation of equal molecular quantities of a p. diamine and a phenol, in alkaline solution; or by the conjoint oxidation of a p. amido-phenol and an amine. Finally, as in the case of Indamines, the p. phenylenediamine (or dimethyl-p-phenylenediamine) can be replaced by nitrosodimethylaniline.

The only Indophenol met with in commerce was obtained by O. N. Witt and H. Koechlin from nitrosodimethylaniline (or dimethyl-p-phenylenediamine) and α -naphthol; it, therefore, has the following formula:—



By reduction it is converted into a leuco compound,



which can be readily retransformed into the dye-stuff by oxidation. This property forms the basis of its application in the so-called Indigo-indophenol vat, and in calico printing.

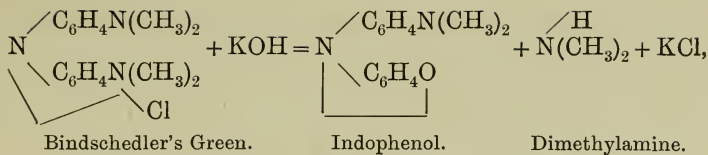
So far as we have gone in the study of dye-stuffs, Indophenol is the first example of those for which the textile fibres exhibit no affinity, a circumstance attributable to its chemically indifferent character. Indophenol White, or the leuco compound of Indophenol, on the other hand, exhibits an acid, phenol character, and, therefore, has an affinity for the textile fibres.

Like the Indamines, **Indophenol Blue** is very susceptible to acids, and is decomposed by them in the same way. This circumstance has retarded the use of Indophenol Blue in printing and dyeing, for which purposes (calico printing in particular) it is otherwise well adapted by reason of the indigo shade, washing-fastness and cheapness of its dyeings. It is also very susceptible to the influence of steam.

If nitrosophenol be allowed to act on an alkaline solution of phenol an Indophenol is again produced, quinonephenol-

imide, $\text{N} \begin{array}{l} \diagup \text{C}_6\text{H}_4\text{OH} \\ \diagdown \text{C}_6\text{H}_4\text{O} \\ \hline \end{array}$ (?), which is therefore a derivative of di-
p.-oxydiphenylamine.

The Indophenols can also be prepared from the Indamines, a circumstance sufficient to reveal the relation between these two classes of dye-stuffs. Thus, Bindschedler's Green, under the influence of an alkali, furnishes an Indophenol:



dimethylamine being eliminated.

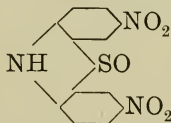
Latterly, a new sphere of utility has been opened up for the Indiphenols in the manufacture of sulphur dyes (Immediate Pure Blue).

THIAZINES, OR LAUTH'S DYE-STUFFS.

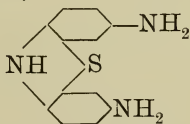
If a solution of p. phenylenediamine, containing sulphuretted hydrogen, be oxidised with ferric chloride, there results a violet dye-stuff, which has received the name of Lauth's Violet after its inventor (1876). Its constitution, and that of the other members of the same series, was determined by Bernsthen in the following manner. The action of sulphur on diphenylamine furnishes thiodiphenylamine,



which, on nitration, yields a paradinitro product,

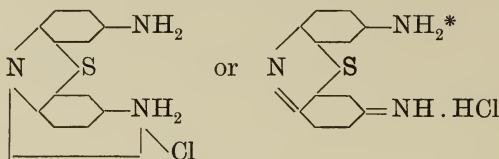


and this in turn is transformed by reduction into di-p.-amidothiodiphenylamine,



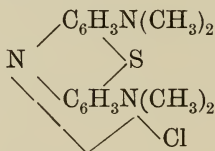
This latter compound is identical with the leuco base of Lauth's Violet, and is also converted into that dye-stuff on oxidation.

Consequently, Lauth's Violet—or rather, its chloride—has the following constitutional formula:—

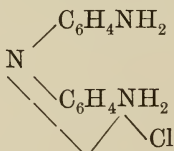


It is a handsome dye-stuff, but, by reason of its high price, has never met with any practical application.

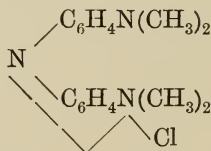
By applying the above reaction to dimethyl-p.-phenylenediamine, or by oxidising the base formed by the action of sulphuretted hydrogen on nitrosomethylaniline, Caro succeeded in obtaining a valuable dye-stuff, **Methylene Blue** (1887), which has the formula:—



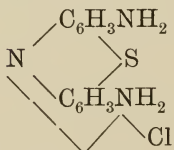
It therefore stands in the same relation to Lauth's Violet as Bindschedler's Green does to Phenylene Blue, as may be seen from the subjoined formulæ:—



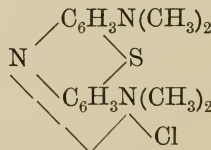
Phenylene Blue.



Bindschedler's Green.



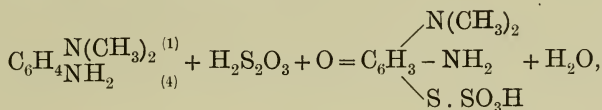
Lauth's Violet.



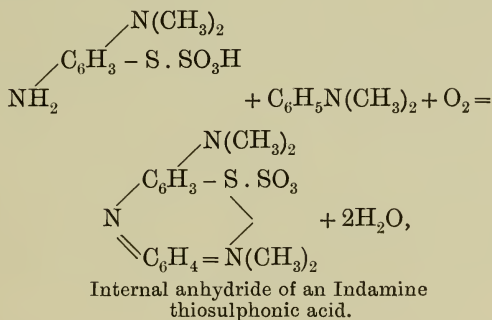
Methylene Blue.

* For another conception of this constitution, see Safranin.

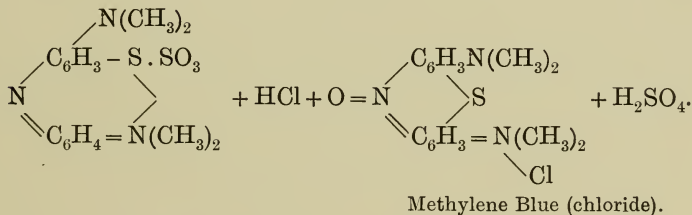
At the present time, Methylene Blue is produced solely by the so-called "Thiosulphate process," *viz.*, by oxidising dimethyl-p.-phenylenediamine and dimethylaniline in the presence of sodium thiosulphate and zinc chloride. The first product of this reaction is probably a thiosulphonic acid of dimethyl-p.-phenylenediamine :



which condenses with the dimethylaniline, to form a thiosulphonic acid of an Indamine :



which latter is converted, by the action of an acid and oxygen, into Methylene Blue :



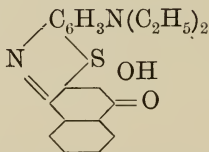
The procedure may be modified by treating an Indamine with an oxidising agent in presence of thiosulphate, thereby forming a thiosulphonic acid, which can then be converted into Methylene Blue in the same manner as before.

Indophenols can also be converted into Thiazines in an analogous manner, by preparing the corresponding thiosulphonic acid and treating the same with a strong acid.

The superiority of the thiosulphate process over the older method consists in the fact that one half the more expensive dimethyl-p.-phenylenediamine is replaced by the cheaper dimethylaniline. Moreover, the new process gives a higher yield and a purer product.

Methylene Blue is generally met with in commerce in the form of a double compound of zinc chloride, and of variable purity; and is of great importance in cotton dyeing and calico printing. It is fixed by the aid of tannin. For wool dyeing it is not very well adapted, being in this case extremely sensitive to light; neither is it used for dyeing silk. On cotton it is much faster than most Aniline dye-stuffs, and is specially suitable for the production of sky-blue tints. Nitric acid converts it into a green dye-stuff, Methylene Green, which is probably a nitrated Methylene Blue.

Brilliant Alizarine Blue (By.). — This dye-stuff is an oxynaphthoquinonimide derivative corresponding to the formula



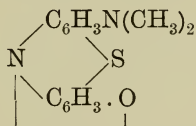
It is prepared by bringing β -naphthoquinone (or its sulpho acid)* into contact with nitrosodiethylaniline in presence of sodium thiosulphate and acetic acid. The product is extremely fast, and, being cheap, competes successfully with Anthracene Blue and the Alizarinecyanines. It is used in the form of chrome lake, principally for wool dyeing, though the mark 81 is also suitable for printing.

* When such an acid is employed, the sulpho group is eliminated during condensation.

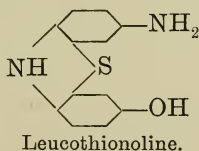
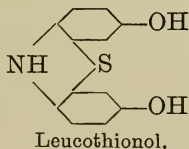
To the Thiazines also belong **New Methylene Blue** and **Thiocarmine** (Cassella). The first of these is a Methylene Blue prepared with nitrosoethyl-o.-toluidine instead of nitroso-dimethylaniline. It has a redder tinge, and is faster to acids, though less fast to alkalis than the latter; several of the marks are mixtures. For some time a dye-stuff of different constitution (see Oxazines) was sold as New Methylene Blue. **Thiocarmine** is a benzylated sulphonic acid of Methylene Blue, and serves as an acid dye-stuff in wool dyeing, replacing the less washing-fast Indigocarmine. In consequence, however, of its great sensitiveness to light, it is now very little used.

The Thiazines are much faster, especially to acids, than the Indamines and Indophenols, a circumstance apparently attributable to the formation of the ring by the electronegative substance, sulphur.

The thioderivatives corresponding to the Indophenols are obtained from the Thiazines by boiling with alkali, and are termed **Thionolines**. Thus, Methylene Blue furnishes a dimethylthionoline, **Methylene Violet**:



By treating hydroquinone and p. amidophenol (or p. phenylenediamine) with sulphur, Vidal obtained a **Leucothionol** and **Leucothionoline**:

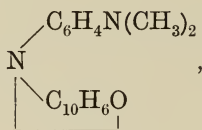


Methylene Grey (M. L. Br.) is a mixture (see Dye-stuffs of Unknown Constitution).

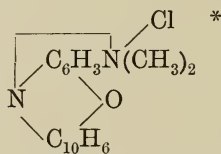
OXAZINES.

By heating 1 molecule of β -naphthol with 1 molecule of nitrosodimethylaniline chloride, dissolved in glacial acetic acid, Meldola, in 1879, obtained a blue dye-stuff, which, like all these prepared in the same manner, was known by the group name of "Meldola's Dye-stuffs". At the present time, their constitution being known, they are termed Oxazines.

To this class belong a number of, mostly blue to violet, dye-stuffs which were formerly in extensive use for dyeing and printing cotton, and are much faster, especially to acids, than the Indophenols. The only difference in constitution between them and these latter is in the mode of connection of the oxygen and the nitrogen atoms, as a glimpse at the subjoined formulæ will show:—



Indophenol.



Meldola's Blue (hydrochloride).

The latter formula also shows that the Oxazines differ from the chemically inert Indophenols by possessing a decidedly basic character.

Meldola's Blue is met with in commerce, as a hydrochloride, or a double compound of zinc chloride, under the names: New Blue (C., By.), Naphthalene Blue R in crystals (By.), Cotton Blue R (B. A. S. F.), Fast Blue 2B for cotton, Naphthol Blue, etc. It has the defect of being sensitive to alkalis.

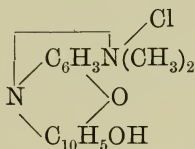
According to a process patented by the Hoechst Farbwerke, the Oxazines can also be produced on the cotton fibre. A

* For another conception of this formula, see Safranine.

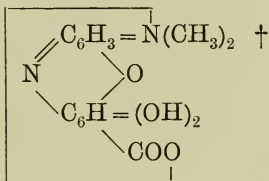
solution of the components, in conjunction with oxalic acid and tannin, is printed on the fabric, and the formation of the dye-stuff is effected by steaming. As has been shown by V. Fussgaenger,* the combination of nitrosodimethylaniline and resorcine is the most suitable for this purpose. The **Nitroso Blue** produced in this manner is a dye-stuff of great technical importance, on account of its handsome indigo shade and great fastness.

Other dye-stuffs of this group are :—

Muscarine (Durand and Huguenin), prepared from nitrosodimethylaniline and 2. 7. dioxynaphthalene :



also **Gallocyanine**, or “violet solide,” which is obtained by heating nitrosodimethylaniline and gallic acid, the constitutional formula being therefore :—



Gallocyanine is a mordant dye-stuff, and its chrome lake is employed, as a fast violet dye in wool dyeing, for bottoming Logwood. It is also largely used in calico printing. Closely allied dye-stuffs are: Gallocarmine Blue (Gg., By.), from gallamic acid, $C_6H_2(OH)_3CONH_2$, and nitrosodimethylaniline; also Celestine Blue, prepared in the same manner from nitrosodi-

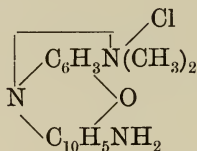
* Other dye-stuffs of this nature have been described by Fussgaenger (Dissertation, Basle, 1900).

† Internal saline combination is therefore assumed.

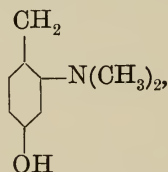
ethylaniline. Both products are mordant dye-stuffs, furnishing clearer dyeings than Gallocyanine. Sulphonated Gallocyanines (D. H.) are acid and mordant dye-stuffs.

An ether of Gallocyanine is sold by Sandoz & Co., under the name of Prune.

Nile Blue * (B. A. S. F.) is a tannin dye-stuff, distinguished for the special purity of its dyeings. It is prepared from nitrosodimethylmetamidophenol and naphthylamine, and has the formula :—



Of similar character are **Capri Blue** and **Cresyl Blue** (Leonhardt), the former being prepared from nitrosodimethylaniline and dimethyl-m.-amidocresol :



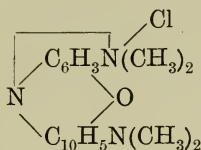
and being very fast to light, but expensive. Cresyl Blue has but little practical importance.

Cyanamines.—This name is applied to the dye-stuffs, first prepared by Witt, obtained by the action of alcoholic potash on Oxazines. They are fast “night blues,” of purer and more greenish shade than the corresponding Oxazines. At the present time they are prepared by acting on Oxazines with amines. Included in this class are :—

New Methylene Blue (C.), which is obtained by the action

* The mark BB, a benzylated Nile Blue, is so sensitive to alkalis as to be suitable for testing the resisting power of glass.

of dimethylaniline on New Blue, and is therefore a dimethylated Nile Blue, corresponding to the formula :—



Fast Green M (D. H.) is prepared from Muscarine and Aniline.

Dolphin Blue (Sandoz and By.), obtained by sulphonation from Gallocyanine and Aniline, is a mordant dye-stuff used in calico printing on account of its handsome, clear shade.

A similar product is Gallanilindigo or Tannin Indigo (D. H.), which, on nitration, furnishes Gallaniline Green, or Solid Green G (D. H.).

Other dye-stuffs of this group have been prepared within the past few years by the action of phenols, sulphurous acid and benzhydrols on Oxazines. The phenocyanines (D. H.), which are obtained from Gallocyanines and phenols, enjoy great favour for calico printing.

Certain blue dye-stuffs obtained by the action of sulphurous acid on Gallocyanines, are met with under the names Chromocyanine, Brilliant Gallocyanine, and Indalizarine (D. H.).

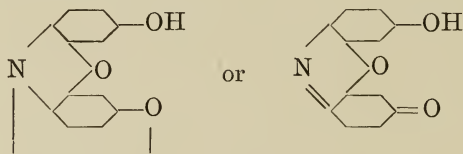
According to a discovery made by Fr. Bayer & Co., and subsequently confirmed by Moehlau, tetralkyldiamidobenzhydrol condenses with Oxazines to form new dye-stuffs (Bayer's New Fast Blue), water being eliminated.

Weselski's dye-stuffs.—Some years ago, Weselski, by acting with nitrous acid on an ethereal solution of resorcline, obtained a dye-stuff, which he regarded as a diazo compound, and, therefore, named Diazo-resorcline. By heating this product with concentrated sulphuric acid, he obtained Diazo-resorufine, which, when dissolved in alkali, gives a bluish-

red solution with a handsome vermilion red fluorescence. A hexabromo derivative of Diazo-resorufine has been put on the market, under the names Resorcine Blue, Fluorescent Blue, by the Ges. f. Chem. Indust. Basle, as a dye-stuff for silk.

Finally, by heating Resorcine with sodium nitrite, Benedikt and Julius obtained a dye-stuff, which, in consequence of its great sensitiveness to acids, finds employment as an indicator, under the name Lackmoide.

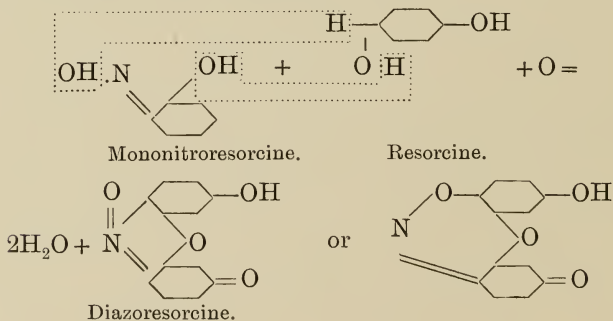
These technically unimportant dye-stuffs have recently been identified by Nietzki as Oxazines or Oxazones. According to this worker, Weselski's Diazo-resorufine has the following constitution:—



in accordance with which view it would, therefore, be an Oxazone analogous to quinonephenolimide.

Oxazones of the naphthalene series have latterly been prepared by Kehrman.

Nietzki obtained Diazo-resorcine by the oxidation of an alcoholic solution of Resorcine and mononitroresorcine with manganese peroxide and sulphuric acid, and, therefore, gave it the following constitutional formula:—



Liebermann's Dye-stuffs.—This name is applied to the coloured products formed by the action of nitrosophenols on phenols dissolved in concentrated sulphuric acid. They are also obtained by acting on phenols with nitrobenzol, by heating the p. amidophenolsulphonic acids, and by the action of brominated nitro-hydrochloric acid on phenols. They are allied to the Weselski dye-stuffs, and, therefore, also belong to the Oxazines, but have not found any technical application. Brunner and Ph. Chuit, who have discovered the various modes of formation of these dye-stuffs, propose to call them Dichroines, on account of their dichroic properties and beautiful fluorescence.

THE AZINE GROUP : EURHODINES, SAFRANINES, AND INDULINES.

CONSTITUTION AND HISTORY.

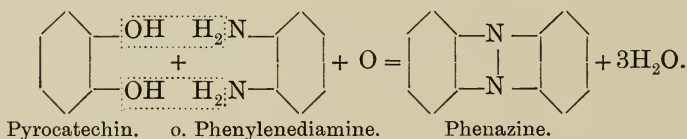
Although many of these dye-stuffs, especially those belonging to the Safranines, were known already in the early days of the coal-tar industry, their constitution remained unknown for a long time.

The first coal-tar dye-stuff, Mauveine, was prepared by Perkin in 1856; and in its production a dye-stuff belonging to the Safranines was obtained as a waste product. In order to obtain this Safranine from aniline, attempts were made with a number of oxidising agents, by various workers; but the first rational method was that of Felix Duprey, who, in 1865, took out a French patent for the oxidation of aniline with lead nitrate in acetic solution.

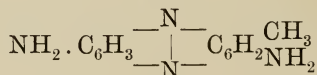
On a manufacturing scale, Safranine was first produced and put on the market by Lotz, of Basle (1868). It was afterwards manufactured also in France and Germany.

Although various methods of preparing Safranine were introduced in rapid succession, and at the same time frequent attempts were made to discover its constitution, the latter continued to remain problematical for a long time. The discovery of the Eurhodines by Witt, and the accurate recognition of their constitution, as well as their close relationship with the Safranines; and the discovery of the Indamines and their connection with the Safranines; formed the first means enabling an approximately true formula to be constructed for the last named.

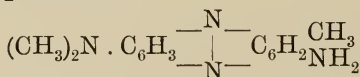
First, as regards the Eurhodines, their constitution was determined in the following manner. By heating pyrocatechin with *o.* phenylenediamine, Merz and Ris obtained phenazine:



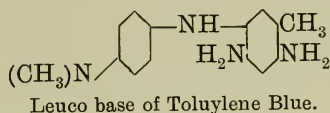
In a similar manner, pyrocatechin and *o.* toluylenediamine furnished methylphenazine. The constitution of these compounds is revealed by their mode of formation. It was then proved that a Eurhodine already known, was derived from the foregoing methylphenazine. The simplest Toluylene Red, already mentioned in speaking of the Indamines (*q.v.*), was converted by Bernthsen and Schweitzer into methylphenazine by the elimination of two amido groups, and was therefore identified as a diamidomethylphenazine,



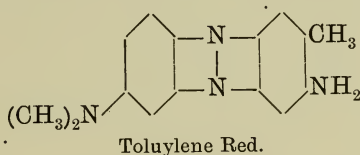
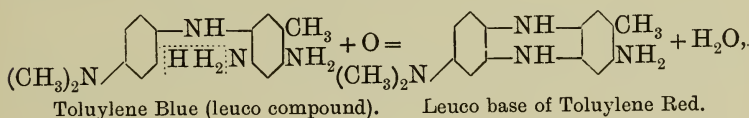
Toluylene Red must consequently be regarded as a dimethyldiamidomethylphenazine,



and its formation from Toluylene Blue can be explained by the assumption that one amido group of the meta-diamine is in the ortho position to the connecting nitrogen :—



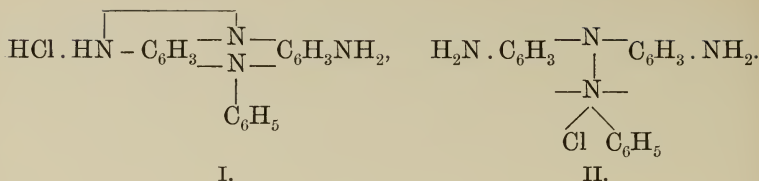
and that, in the subsequent oxidation and formation of Toluylene Red, this amido group engages in the corresponding ortho position of the second nucleus :—



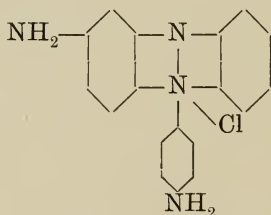
On the other hand, the Indamines were found to play an important part in the formation of the Safranines; according to Witt, they occur as intermediate products, and Andressen reports that they can be converted into Safranines by conjoint oxidation with a monamine. Finally, Nietzki discovered that the Safranines contain the diphenylamine radicle.

In order to take into account these facts, and the similarity between the Safranines and the Eurhodines, it must be assumed that the former are produced from an Indamine and monamine in such a manner that two benzol nuclei are connected together by two nitrogen atoms.

The following constitutional formulæ were constructed by Bernsthen for the chloride of the simplest Safranine :—



Both formulæ, however, correspond with the previously discovered fact that two amido groups are present in Safranin; but since both these groups are assumed to be capable of diazotisation, the second formula alone suffices to explain the constitution. This is, however, opposed by the circumstance that this formula does not account for the existence of two isomeric diethyl ethers, as found by Nietzki; so that finally a decision was made in favour of Witt's proposition to assume an asymmetrical formula for Safranin, as satisfactorily explaining all the facts :—

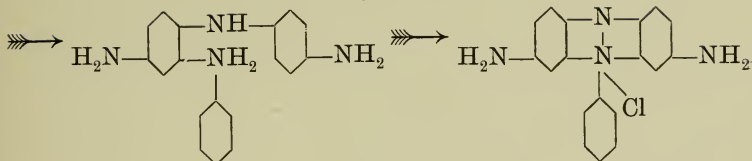
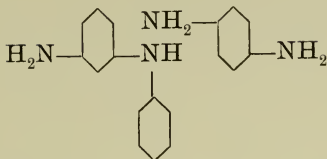


Witt's Safranin formula.

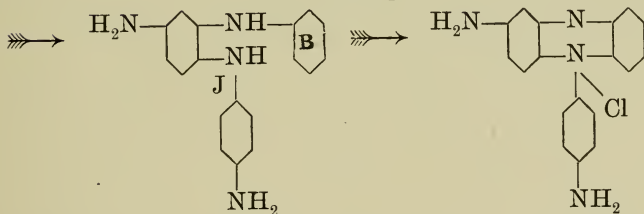
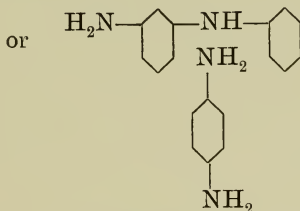
After this formula had held the field for a long time, it was recently discovered, by G. Koerner and Schraube, to have been based on an error, inasmuch as the two aforesaid diethylsafranines are identical, and not different. Moreover, it has been definitely shown, by the synthesis of several safranin derivatives, that the symmetrical formula alone is capable of expressing the facts of the case.

As the subjoined formulæ will show, the condensation of m. amidodiphenylamine might proceed in two different ways :—

I.



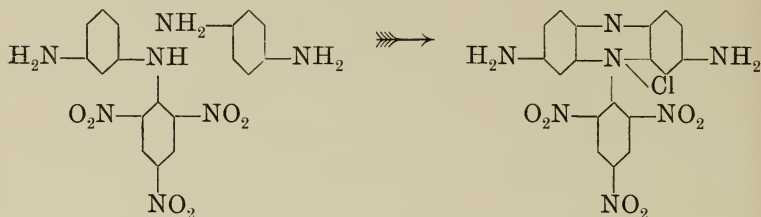
II.



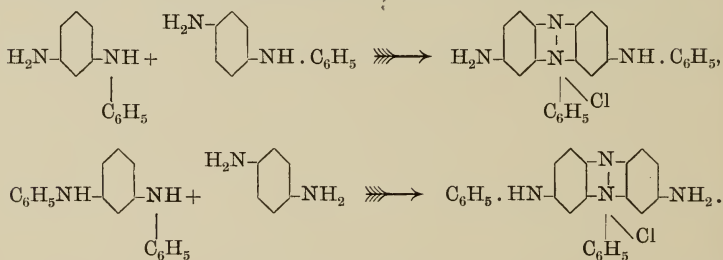
In the second instance exemplified above, which leads to an asymmetric formula, the Indamine nitrogen (indicated by J) must, therefore, engage in the free benzol nucleus (marked B) of the diphenylamine radicle. Since, however, on replacing this benzol nucleus by methyl—*i.e.*, by using methyl-m.-phenylenediamine instead of phenyl-m.-phenylenediamine—a Safranin is produced (Jaubert), it follows that the reaction can only proceed in the manner expressed by the formula I.

A Safranin is also formed when the diphenylamine derivative, obtained from picryl chloride and m. phenylenedi-

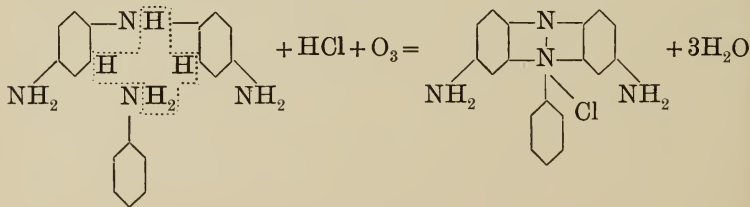
amine, is oxidised in conjunction with p. phenylenediamine (Jaubert), a result which also points to a symmetrical formula :—



Finally, also, Nietzki, the most strenuous defender of the asymmetrical formula of Safranin, has contributed a synthetical proof of its inaccuracy. By the condensation of phenyl-m.-phenylenediamine and phenyl-p.-phenylenediamine on the one hand, and from diphenyl-m.-phenylenediamine and p. phenylenediamine on the other, he obtained one and the same Phenylsafranin, a result solely explicable by the assumption of a symmetrical formula for Safranin :



Consequently, bearing in mind the intermediate production of Indamine, the formation of Safranin may be represented in the following manner :—



Hence the Safranines are formed by the conjoint oxidation of 1 molecule of a paradiamine and 2 molecules of a monamine; and the conditions under which this result becomes possible, are—in harmony with the above formula—as follows:—

1. Only a single amido group may be substituted in the employed paradiamine, the Indamine nitrogen being then supplied from the second group, which is free.

2. One molecule of the employed monamine (or the first one to enter into the reaction) must have the para position to the amido group unoccupied, in order to render possible the engagement of the one amido group of the diamine, or, in other words, the production of the Indamine.

3. The second monamine, or the second molecule of the monamine employed, must be primary.

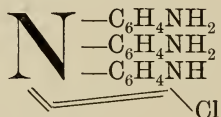
The foregoing condensed *résumé* of the scientific investigation of the Safranines only gives an incomplete picture of the difficulties encountered in that task. The various methods of producing Safranines, such as Caro's, which consisted in treating p. toluidinazoorthotoluidine and o. toluidinazoorthotoluidine with a little nitric acid; further, that consisting of acting with o. toluidine chloride on the amidoazotoluol from o. toluidine; and the formation of Safranine by the oxidation of a mixture of p. toluylenediamine and toluidine—were puzzling, whereas we now explain the formation of Safranines from amidoazo bodies by a decomposition into paradiamines and monamines. True, these different methods of formation led to the construction of constitutional formulæ for Safranine; but a special part was ascribed in the same to the methyl groups of o. toluidine, an error first revealed by Witt, in 1878, preparing a Safranine, the so-called Phenosafranine, from p. phenylenediamine and aniline.

The additional discovery that p. phenylenediamine will not give Safranines, either with p. toluidine (Witt), or with

secondary and tertiary bases (Nietzki), did not throw any further light on the obscure process of safranine formation. Moreover, the important observation, by Witt, that the formation of Safranine goes on in two phases—unstable dye-stuffs (Indamines) being first produced by cold oxidation, and the red Safranines only in the warm—could not at first be utilised, owing to ignorance of the nature of the intermediate products.

The first insight into the constitution of the Safranines was afforded by Nietzki's proof of the formation of Safranine by the oxidation of a mixture of equal molecular proportions of di-*p*-amidodiphenylamine and a primary monamine. It now became justifiable to assume the existence, in Safranine, of two monamine radicles with their benzol nuclei attached to one nitrogen atom. Nietzki next succeeded in identifying the constitution of Bindschedler's Green, Phenylene Blue, and, finally, also Witt's Toluylene Blue, to which he gave the formulæ still accepted.

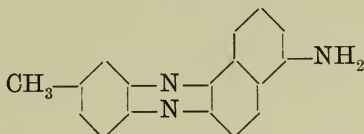
In addition, Nietzki, by the oxidation of equal molecules of diethyl-*p*-phenylenediamine, diethylaniline, and aniline, prepared a tetraethylsafranine, from which the presence of two amido groups in the safranine molecule could be deduced. The new formula then constructed by this worker, for Safranine, or its hydrochloride,



also made allowance for the circumstance that Safranine was regarded as an ammonium base, and presented some analogy with the triphenylmethane dye-stuffs. However, a revision of the empirical formula of Safranine soon revealed the unreliability of Nietzki's hypothesis.

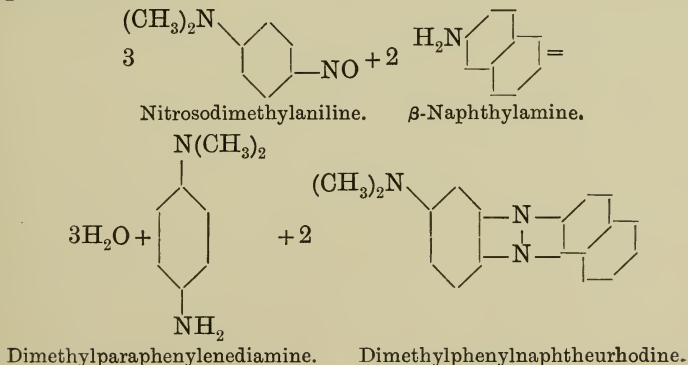
On the other hand, Witt made the observation that amidoazo compounds containing an amido group in the

ortho position to the azo group, do not, as would be expected, furnish compounds of the induline type* with a naphthylamine chloride, but yield products resembling the Safranines in behaviour and allied to the quinoxalines (*q.v.*). To these Witt gave the name Eurhodines, the one formed from amidoazotoluol and α -naphthylamine being credited with the formula :—



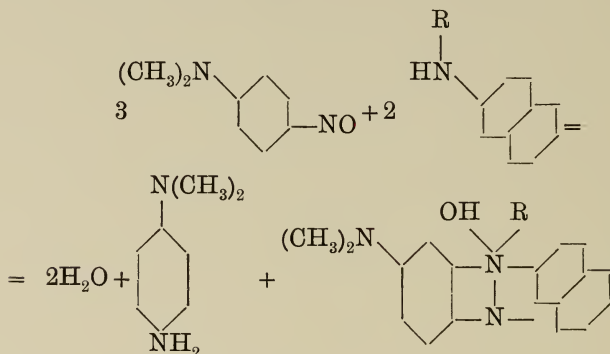
Next ensued the syntheses of the phenazines and metaphenazines by Merz and Ris; the elucidation of the constitution of Toluylene Red by Bernthsen and Schweitzer, and its connection with the Eurhodines; and eventually, as the happy final of the collective researches in this branch, the construction, by Bernthsen, of the two above-mentioned formulæ for Safranine.

The intimate connection between the Safranines and the Eurhodines was experimentally demonstrated by Witt in the following manner. By allowing nitrosodimethylaniline to act on β -naphthylamine, there results a dimethylphenyl-naphtheurhodine :



* Like the corresponding para derivative.

By employing in the place of β -naphthylamine a secondary base derived therefrom, and submitting it to the same reaction, the product will be the "azonium base" corresponding to the above Eurhodine, a Safranine:



At present the formulæ of the Safranines are written somewhat differently (see below), owing to the results of the newer researches on the Indulines, which we shall now proceed to consider.

Indulines, Nigrosines.

Under these titles, and also under the names, Coupier Blue, Fast Blue, etc., have appeared on the market, from the beginning of the aniline dye-stuff industry, a number of violet, blue, to grey dye-stuffs, which, in constitution, are closely allied to the Safranines, and may equally be regarded as diphenylamine derivatives.

In 1863 H. Caro and J. Dale prepared the first Induline by heating aniline chloride with sodium nitrite. It was very soon recognised that the process here involved consisted in the action of aniline chloride on amidoazobenzol, and that the resulting products differed according to the temperature and duration of the heating. Azophenine is the first product, and this, on being heated further, passes over successively into Induline B (or Azodiphenyl Blue) and Induline 3B.

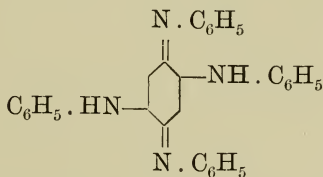
On the large scale the process is performed by heating amidoazobenzol with aniline chloride dissolved in aniline.

As regards the constitution of this dye-stuff, this matter remained in profound obscurity until within a very recent period. All that could be concluded from Witt's observation that the substitution of phenylamidoazobenzol for amidoazobenzol smoothens the course of the reaction and obviates the otherwise invariable liberation of ammonia, being that the diphenylamine radicle is present in Induline.

Through the beautiful researches of O. Fischer and Hepp on the one hand, and of Kehrman and Messinger on the other, a certain insight has now been acquired of the constitution of the Indulines.

The first step in this direction was made by O. Fischer and Hepp, by determining the constitution of Azophenine, a substance that had already been obtained by Kimich from p. nitrosophenol and aniline acetate, and by Witt and Thomas as an intermediate product in the preparation of Induline.

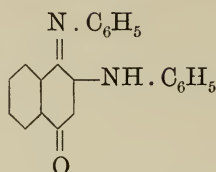
It was identified as a dianilidoquinonedianilide* of the formula :—



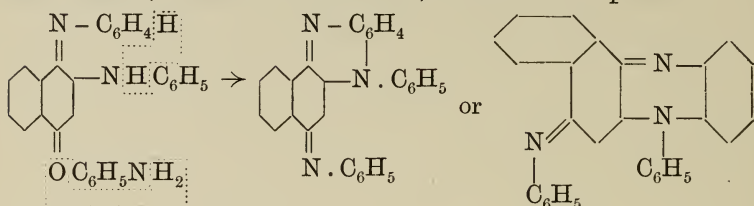
The same compound is also obtained from other nitroso compounds, by heating with aniline and aniline salts.

An analogous naphthalene derivative, which is formed in nearly every reaction leading, in the benzol series, to the production of Azophenine, is anilidonaphthoquinonanilide,

* Azophenine furnishes quinonedianilide on the elimination of aniline, and *vice versâ*; the p. position of the anilido groups was proved by Nietzki and Schmidt.

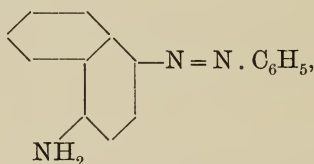


On employing higher temperatures in the preparation of this substance, the quinone oxygen is replaced by the aniline radicle, water is eliminated, and the compound

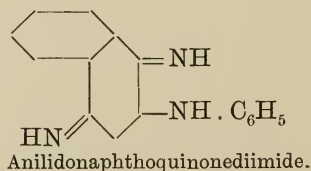
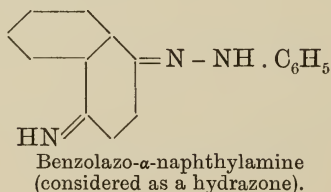


is formed.

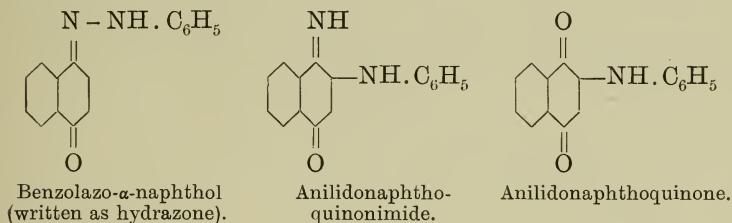
This dye-stuff furnishes red soluble salts, and was christened Rosinduline by its discoverers (Fischer and Hepp). It is also formed from several amidoazo compounds, *e.g.*, benzolazo- α -naphthylamine,



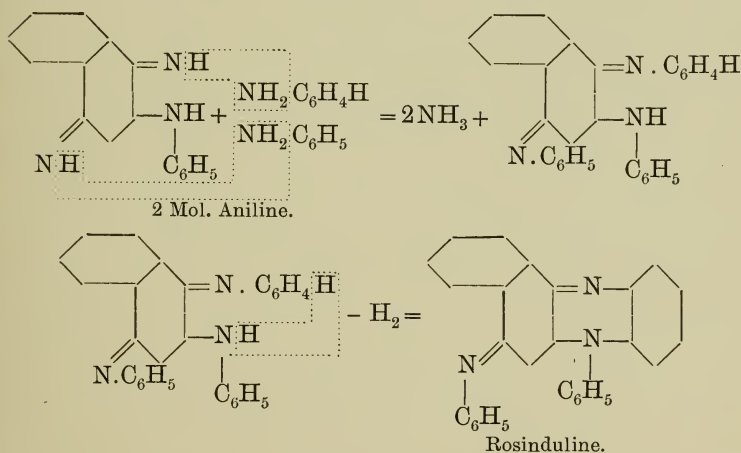
by heating with aniline and aniline chloride. The formation of Rosinduline in this manner is explained by Fischer and Hepp by the assumption that the substances in question are first transformed into the isomeric anilidoquinonediimide—so that one must regard the amidoazo compounds as hydrazones:



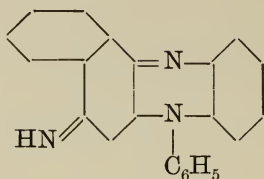
The conditions actually observed are as follows: On heating benzolazo-*a*-naphthol with acetic acid for some time, there results, first of all, anilidonaphthoquinonimide, and then, by the substitution of oxygen for the imido group, anilidonaphthoquinone:



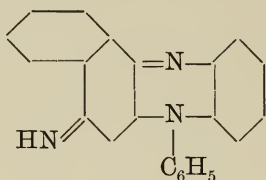
If we now assume, in the case of benzolazo-*a*-naphthylamine, a similar transformation into an anilidonaphthoquinone-diimide, the conversion of this substance into Rosinduline when heated with aniline and aniline chloride can be readily explained, as is evident from the subjoined equation:—



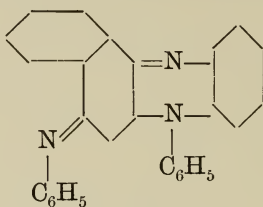
If this reaction be modified, by heating the Benzolazo-*a*-naphthylamine with aniline and alcohol under pressure, the product will be a simpler type of substance containing a smaller proportion of oxygen:—



To distinguish it from this "simplest Rosinduline," the earlier substance has been named Phenylrosinduline :

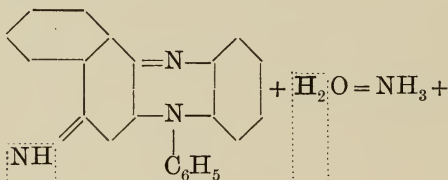


Rosinduline.

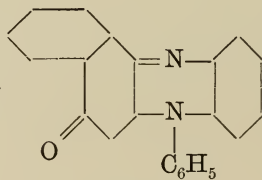


Phenylrosinduline.

When this simplest Rosinduline is heated with concentrated hydrochloric acid, under pressure, the following reaction occurs :—

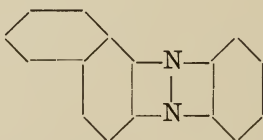


Rosinduline.



Rosindone.

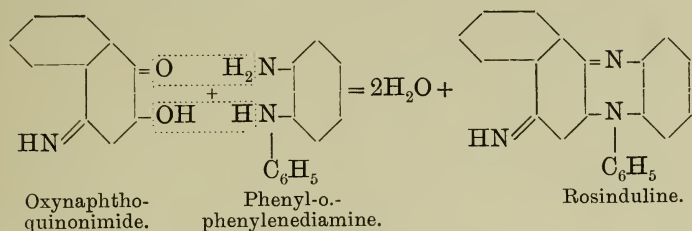
the product, Rosindone, furnishing the well-known *α*-naphthophenazine,



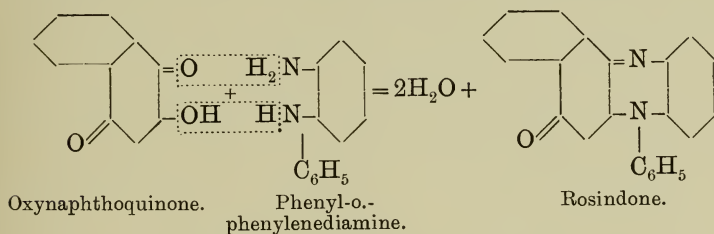
when distilled over zinc dust kept at red heat.

This systematic degradation of Rosinduline demonstrates the accuracy of the constitutional formula already given for same. This is also confirmed by the synthesis of Rosindu-

line, effected by Kehrmann and Messinger, from oxynaphthoquinonimide and phenyl-o.-phenylenediamine :



Rosindone is obtained in an analogous manner from oxynaphthoquinone and phenyl-o.-phenylenediamine :



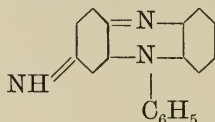
Consequently, Rosinduline appears to be a derivative of p. naphthoquinonimide, from the analogues of which body, in the benzol series, the Indamines, Indophenols, etc., are derived.

Rosindulines are, therefore, formed by the action of naphthalene-azo compounds (or also from nitroso derivatives of the naphthalene series) on aniline and similar bases. Quinoanilides like anilidonaphthoquinonanilide are found as intermediate products, just as in the case of the blue Indulines of the benzol series, dianilidoquinonedianilide (Azophenone) is encountered. In complete analogy with the formation of the blue Indulines from amidoazobenzol is exhibited by that of the Rosindulines from benzolazo-*α*-naphthylamine.

From this extensive analogy in the formation of the Rosindulines and the true Indulines, the conclusion has been drawn that the former are Indulines of the naphthalene

series; in such event the benzol Indulines—*i.e.*, the products derived from the Induline melt, and which will hereafter be called Indulines, for short—must be paraquinoid azines. According to O. Fischer and Hepp, the Indulines must be regarded as anilido derivatives of the Safranines; but a reliable foundation for this hypothesis is still lacking.

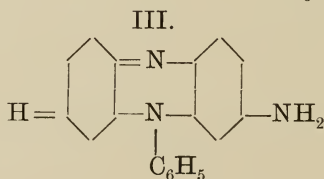
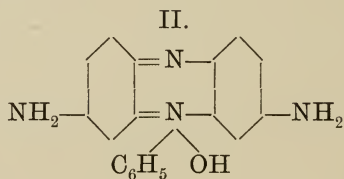
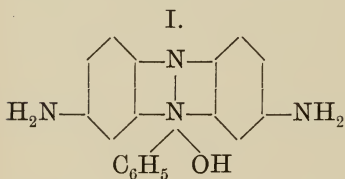
Attempts made to obtain the simplest Induline by heating the Induline melt for a short time with an excess of aniline chlorine, did not succeed, inasmuch as the product, instead of being, as anticipated, the simplest Induline of the formula



was an anilido derivative of aposafranine, the body obtained from phenosafranine by the elimination of an amido group.

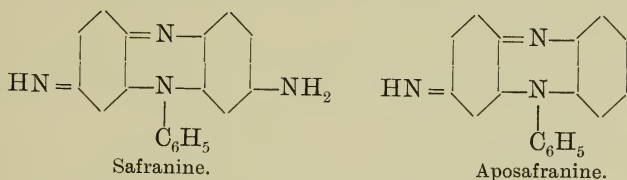
MORE RECENT VIEWS ON THE CONSTITUTION OF THE SAFRANINES.

Within the last few years, the Azines have formed the object of numerous scientific researches by O. Fischer, Hepp, Kehrmann, Nietzki, and Jaubert. The main point of interest to these workers is the query, which of the three subjoined formulæ should be given to Safranine :—



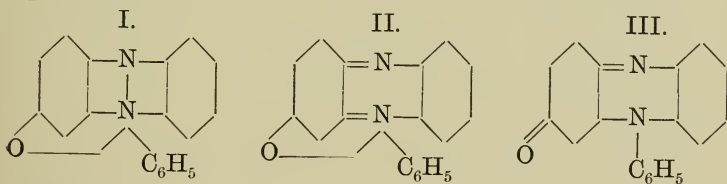
Of the large quantity of accumulated facts brought forward in support of one or another of these formulæ, none but the most important can be mentioned here.

When Safranine is diazotised in the ordinary manner, a monodiaz compound is obtained. This, when treated with alcohol, furnishes the so-called Aposafranine: a substance that does not give any diazo compound, even under prolonged exposure to the action of nitrous acid, and cannot be shown by other means to contain an amido group. Now, this behaviour cannot be explained by either of the formulæ Nos. I. and II., both of which contain two free amido groups. Consequently, Safranine and Aposafranine must be constituted on the lines of the third formula:—

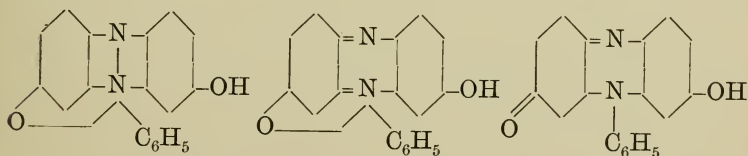


Analogous behaviour is exhibited by the corresponding hydroxyl derivatives, Aposafranone and Safranone:—

Aposafranone:—



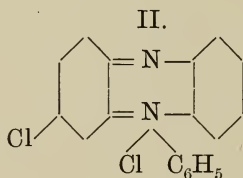
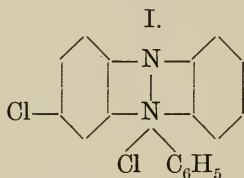
Safranone:—



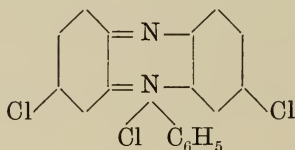
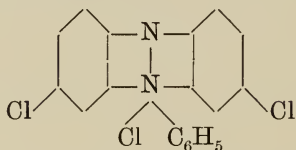
Only a single hydroxyl group can be detected in Safranone, and none at all in Aposafranone; and neither contains an

ammonium hydroxyl. Hence, if one desires to express their constitution by the Safranine formulæ Nos. I. and II., it is necessary to assume dehydration as having occurred between the hydroxyl group and the azonium group—as is done in the above formulæ.

By dissolving these two substances in phosphorous oxychloride, and allowing them to stand in presence of phosphorous pentachloride, O. Fischer and Hepp obtained highly interesting chlorine compounds, the composition of which, however, could not be explained by the No. III. formula, since they contained a chlorine atom in a state of loose salt-like combination. According to the formulæ Nos. I. and II., they can be expressed in the following manner:—
From Aposafranine:—



From Safranol:—

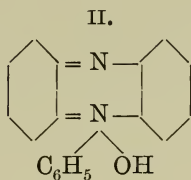
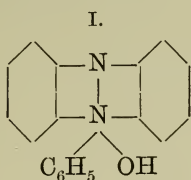


In the trichloro derivative from Safranol, the degree of affinity in the combination is different in each of the three chlorine atoms. As this cannot be explained by the No. I. formula, these chlorine compounds must, therefore, be of orthoquinoid constitution, expressed as by the formula No. II.

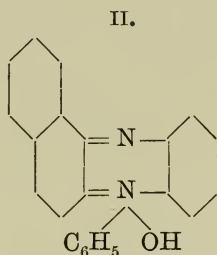
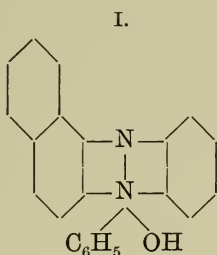
More recently Kehrman has also succeeded in diazotising Aposafranine, by treating its green solution in concentrated sulphuric acid with nitrous acid.* By treating this diazo

* The weak acid solutions of Aposafranine are red in colour.

compound with alcohol, he then obtained an azonium base, phenylphenazonium :



In a similar manner, Rosinduline furnishes naphthophenazonium :



These compounds cannot be of paraquinoid constitution. Neither does the formula No. I. sufficiently express their peculiarities, since it does not reveal their faculty for admitting ready substitution by amines in only one nucleus. Consequently, they have an orthoquinoid structure, in the sense indicated in formula No. II.

These facts are considered by Nietzki and Kehrmann as proving the accuracy of their hypothesis that Safranine is an orthoquinoid azonium base (formula No. II.).

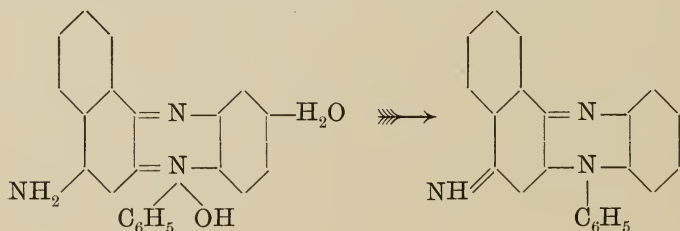
On the other hand, it must be recalled that Safranine contains only one free amido group that can be detected by diazotisation under ordinary conditions ; Aposafraanine none at all. Moreover, the assumption that the green diazotisable solution of Aposafraanine in concentrated sulphuric acid, contains the same substance, in constitution, as is present in a weakly acid, red coloured, and non-diazotisable solution of Aposafraanine, does not seem admissible without further

proof. According to the researches of Jaubert,* the water content, which Nietzki regarded as supporting the orthoquinone formula of the Safranine base, really argues against that formula, since the base in question loses a considerable proportion of this water when dried, and, in fact, can be obtained in a perfectly anhydrous condition by repeated recrystallisation from hot water. Furthermore, Indazine, a dye-stuff prepared in an entirely analogous manner, is perfectly anhydrous, and therefore is a derivative of p. quinonimide.

Consequently, in view of the facts thus displayed, Safranine must be regarded as a paraquinone derivative, like Rosinduline, in the sense implied by O. Fischer, Hepp and Jaubert.

That Safranine derivatives can also exhibit orthoquinoid constitution, has been shown already. Moreover, Kehrmann, in the course of his beautiful and comprehensive researches on the Rosindulines, discovered several facts indicating that, under certain circumstances, both Safranines and Rosindulines are tautomeric compounds, which may exist in two forms. Thus, for example, the base of a Rosindone was obtained in two forms (blue and red), which are interconvertible and give perfectly identical salts.

Kehrmann also regards as possible the conversion of the orthoquinone form into the paraquinone condition :—



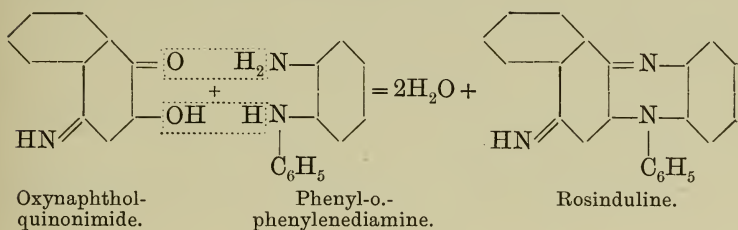
The possibility of such a transformation, or an elimination

* *Berl. Ber.*, 1895, p. 1583.

of water, in the above sense is naturally influenced by the position of the substituent group.

In the case of the Eurhodines, the amido groups of which are readily diazotisable in both nuclei, there is no evident reason for such a constitutional alteration; nevertheless, the Eurhodines seem capable of existing in two forms.

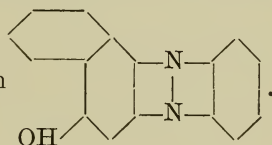
As already stated, oxynaphthoquinimide and phenyl-o-phenylenediamine furnish Rosinduline:



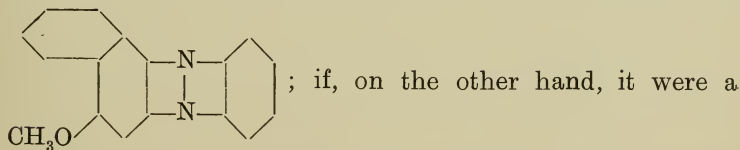
If the two latter components be replaced by non-substituted o. phenylenediamine, we obtain Eurhodine. Hence, on the basis of this synthesis, the Eurhodines must be regarded as paraquinonimide derivatives.

In order to decide this question, Kehrmann and Messinger

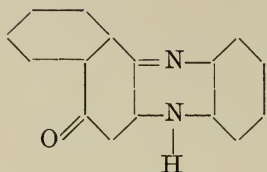
methyated Eurhodol of the composition



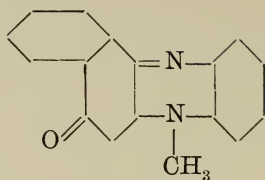
Now, if this really has the formula appertaining to the o. quinonimide form, it would furnish an ether of the formula



paraquinonimide derivative, the following type of methyl ether would be produced:—

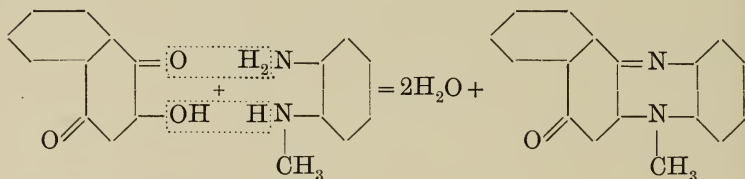


Naphtheurhodol, regarded
as p. quinonimide derivative



its Methyl ether.

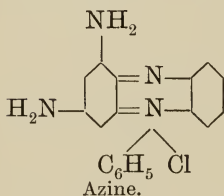
and this ether would be identical with the Rosindone furnished by oxynaphthoquinone and methyl- α -phenylenediamine :



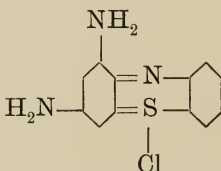
Oxynaphthoquinone. Methyl-o-phenylenediamine.

As a matter of fact, Kehrmann and Messinger found that the methylation of the above Eurhodol furnished two ethers, one of which was identical with the foregoing Rosindone. Hence, α -Naphtheurhodol is a desmotropic substance.

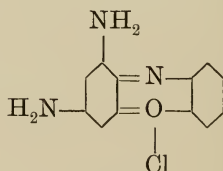
Quite recently Kehrmann* has also proposed the orthoquinone formula for the Thiazines and Oxazines, on the ground of the remarkable similarity between an Azine and the corresponding Thiazine and Oxazine. This formulation involves the assumption of a tetravalent oxygen and a tetravalent sulphur :—



Azine.



Thiazine.

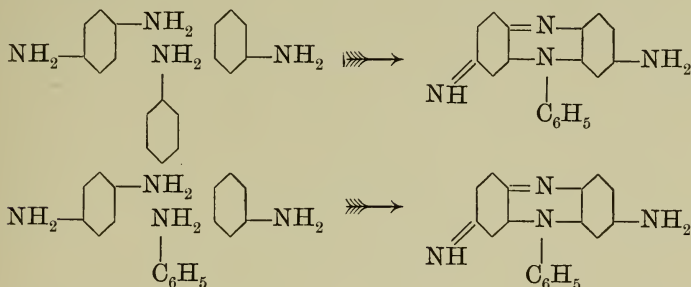


Oxazine.

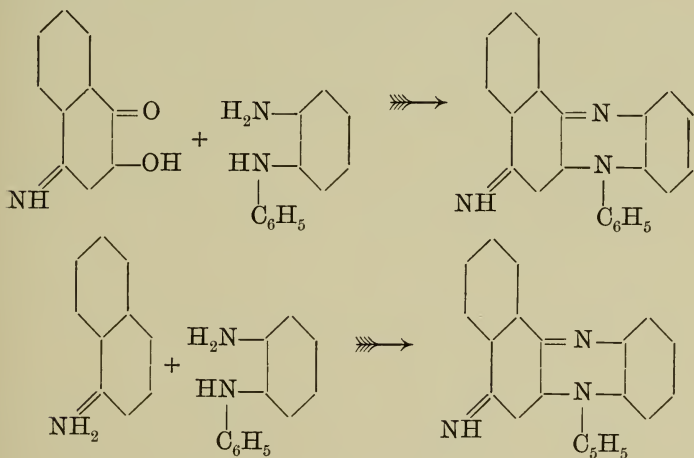
* *Berl. Ber.*, 1899, p. 2601 ; see also Green, *ibid.*, 1899, p. 3155.

FORMATION AND PREPARATION OF AZINES.

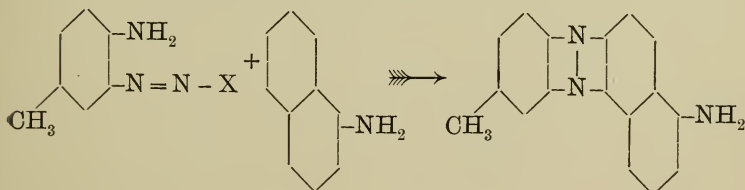
1. From paradiamines, by oxidation with monamines or metadiamines :—

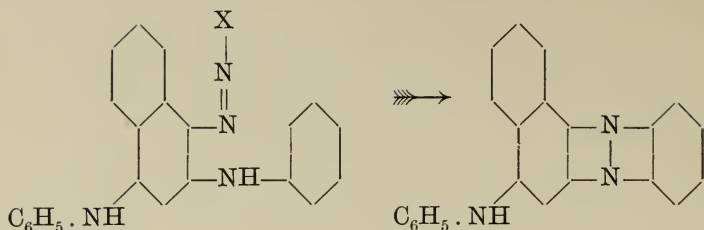


2. From orthodiamines and quinones, oxyquinones, oxyquinonimides, and monamines :—



3. From orthoamidoazo compounds :—

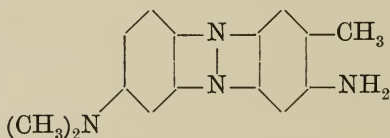




EURHODINES.

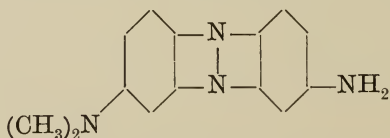
This name was originally applied by Witt solely to the dye-stuffs obtained by acting on α -naphthylamine with ortho-amidoazo compounds. Other methods of preparing them are boiling the aqueous solutions of Indamines containing one free amido group (Toluylene Red); acting with the nitroso derivatives of tertiary amines on metadiamines; condensing orthodioxbenzols (or orthoquinones) with orthodiamines, or the latter with benzolazo- α -naphthylamine, etc.

Neutral Red is the name under which Toluylene Red is placed on the market by L. Cassella & Co.:



It is prepared by acting on metatoluylenediamine with nitrosodimethylaniline chloride.

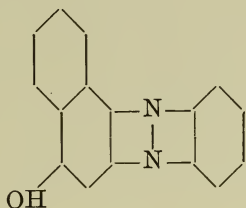
The **Neutral Violet** of the same firm,



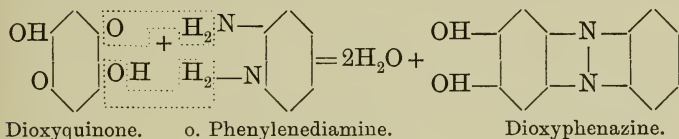
is obtained in a similar manner from metaphenylenediamine.

These dye-stuffs find employment in calico printing.

Eurhodols are acid azines, prepared from the basic forms by sulphonation and subsequent fusion with sodium; or by direct synthesis. Thus Kehrman and Messinger, by condensing oxynaphthoquinone and *o*. phenylenediamine obtained an *α*-naphtheurhodol,



whilst Nietzki and Hasterlik prepared a dioxyphenazine,



in the same way.

None of the Eurhodines has any technical importance.

SAFRANINES.

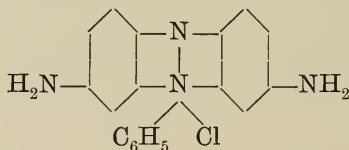
These dye-stuffs are obtained by the oxidation of Indamines in presence of monamines, or—what is really the same thing—by the oxidation of a monamine with the basic mixture required for the production of an Indamine. This is also the usual method of preparation adopted; that they may also be obtained from certain amidoazo compounds (Caro's method, see p. 287) can be explained by assuming the decomposition of these latter into bases suitable for the production of Safranines.

Dye-stuffs of the Safranine type are also now prepared by the condensation of paradiamines with metadiamines, and by the action of monamines on Aposafranine.

Formerly the Safranines were defined as basic tannin dyes, of a more or less yellow tinge, and fluorescent. Their behaviour towards concentrated sulphuric acid was also regarded as characteristic.* More recently, a number of blue Safranines have also become known.

On reduction they furnish leuco compounds, which are readily converted back into dye-stuffs by oxidation in alkaline solution.

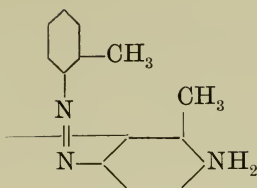
Phenosafranine is the simplest type of Safranine, and was first prepared by Witt, in 1878, from 1 molecule of p. phenylenediamine and 2 molecules of Aniline by oxidation. Its constitution corresponds to the formula



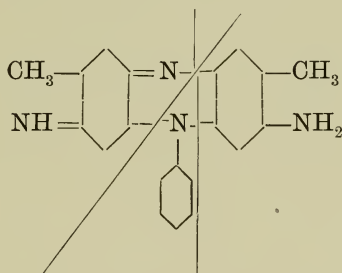
It is merely of theoretical interest.

Safranine.—Various mixtures of tolosafranines and phenotolusafranines are met with in commerce under this name, with different marks (extra G, T, etc.), their composition depending on the materials employed in the preparation. For the most part, Safranine is prepared from an aniline oil, rich in orthotoluidine (aniline for Safranine), or from the basic mixture distilling over during the manufacture of Fuchsine. The action of nitrous acid furnishes the azo compound

* When concentrated sulphuric acid is added to a solution of Safranine, the red colour changes successively into violet, blue, and green; on then adding water, the same changes occur in the reverse direction.



which, by reduction with zinc dust, is decomposed, in the direction shown by the line, into p. toluylenediamine and o. toluidine. Assuming that aniline takes part in the subsequent oxidation with potassium bichromate, a Safranin of the following composition must be formed:—



the method of formation being indicated by the lines drawn across the formula.

If the aniline be replaced by monoalkylorthotoluidine in this reaction, a Safranin of very clear shade is produced.

Safranin has recently been found to be poisonous,* lining-material dyed therewith having produced a peculiar eruption on the skin.

In combination with sundry dye-stuffs, such as Methylene Blue, Safranin is fairly fast, and is largely used in cotton dyeing and calico printing.

When Safranin is diazotised, and then exposed to the action of β -naphthol, it furnishes an azo dye-stuff, exhibiting

* According to Th. Weil (*Zeits. f. Hygiene*, 1891, p. 35), 0.05 gramme of Safranin hydrochloride per kilogramme of body weight is a fatal dose for dogs, when administered as a subcutaneous injection.

the properties of a basic dye, and distinguished by the indigo shade and great fastness of its cotton dyeings. This important dye-stuff, which was introduced by Kegel (Beyer and Kegel of Leipzig), was first brought on the market by the Badische Anilin- und Sodafabrik, in the form of a soluble chloride, and under the name **Indoine Blue**.

Identical therewith are: Naphthindone Blue BB (C.), Diazine Blue BR (K.), Bengaline Blue (a mixture of Indoine and Methylene Blue) (K.), Janus Blue (M. L. Br.), and Indoine Blue (By.).

Methylindone (C.) is an Indoine Blue prepared with amidonaphthols.

According to a patent of the Hoechst Farbwerke, faster dye-stuffs are obtained by the combination of 1 molecule of β -naphthol with 2 molecules of diazosafranine.

Diazine Green (K.) and Janus Green (M. L. Br.) are unimportant dye-stuffs, obtained by the combination of dimethylaniline with diazosafranine.

Diazine Black (K.) and Janus Grey (M. L. Br.) are prepared by the action of phenol on diazosafranine.

Finally, blue basic dye-stuffs are obtained by the action of aldehydes and ketones on singly alkylated Safranines.

Methylene Violet (D. H.), Giroflé, Tannin Heliotrope (C.), is produced by the action of nitrosodimethylaniline chloride on a mixture of the chlorides of m. and p. xyloidine.

Safrosoanilines are obtained when an Indamine is oxidised along with diamidodiphenylmethane.

A number of red and blue azines are obtained from nitrosoanilines and phenylated (or naphthylated) m. diamines, or phenylated naphthylenediamines. They may be regarded as phenylated (or naphthylated) Safranines. Of this class are: Mauveines, Indazine, Basle Blue, Naphthazine Blue, etc. The similarly constituted Rhodulines are obtained in an analogous manner.

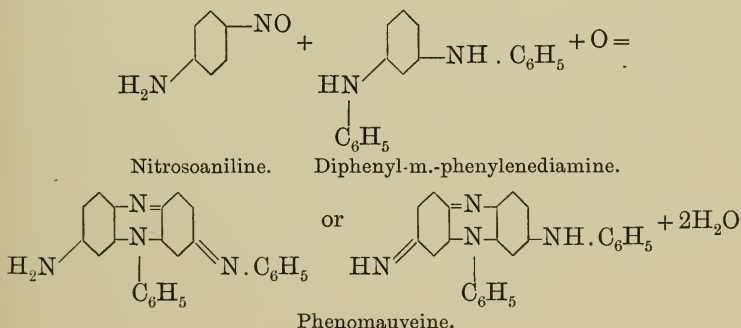
Naphthazine Blue is an acid dye-stuff, but all the others are basic.

Mauveine.—In the hope of obtaining quinine by artificial means, Perkin, in 1856, oxidised allyltoluidine and afterwards aniline, and thereby obtained a violet dye-stuff. At the close of the year 1857, this was put on the market in the form of an alcoholic solution, being known as Mauve in England, and as Aniline Violet or Perkin's Violet on the Continent. At the present time it is called Mauveine.

Mauveine was the first of the aniline dye-stuffs to be prepared on a manufacturing scale, and gave an impulse to the discovery of others; it is therefore of great historical interest, though it never attained any high degree of practical importance. At present it is used to only a small extent, in the form of sulphate, Rosolan, for bluing white silk and for printing postage stamps.

Until very lately the constitution of the mauveine class of dye-stuffs was unknown; and we are indebted to O. Fischer and Hepp for determining same.

This constitution is revealed by the synthesis of the simplest Mauveine, **Phenomaueine**,* which was prepared by Fischer and Hepp from nitrosoaniline and diphenylmeta-phenylenediamine:

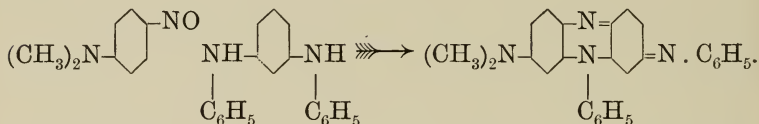


* Perkin's Pseudomaueine, which he obtained by the oxidation of aniline.

The latter formula is the more probable one, because no amido group has been detected in Phenomauveine.

Indazine (C.) is a very clear, bright blue, distinguished by special fastness to alkalis. It is very largely used for topping vat blue on linen, but has been appreciably superseded by Indoine Blue.

It is prepared from nitrosodimethylaniline and diphenyl-m.-phenylenediamine, and is therefore a dimethylphenomauveine :

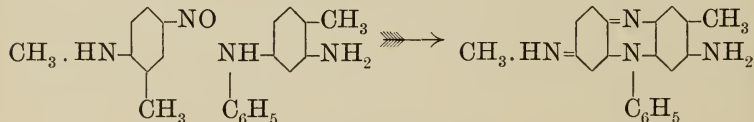


Basle Blue (D. H.) is a dye-stuff similar to Indazine, and gives still clearer dyeings. It has been almost entirely displaced by Indoine Blue. It is prepared from nitrosodimethylaniline and ditolyl-2. 7.-naphthylenediamine.

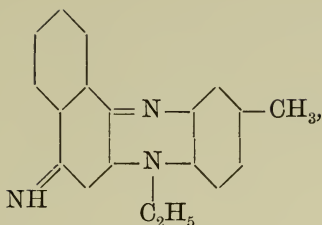
Naphthazine Blue (D. and M. L. Br.) is a cheap blue of good covering power, and can also be fixed with mordants. It competes with Sulphocyanine (By.) for wool dyeing, but is less fast than the latter.

Brilliant Blue (D.) is Naphthazine Blue mixed with Naphthol Black. Naphthazine Blue is prepared from nitrosodimethylaniline and a disulphonic acid of β -dinaphthyl-m.-phenylenediamine.

Rhodulines are very clear red tannin dye-stuffs. Brilliant Rhoduline is well adapted for staining microscopical preparations. It is prepared on the following lines:—



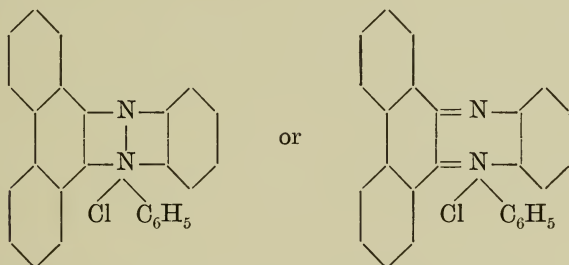
Of the number of dye-stuffs alkylated on the azine nitrogen, patented of late, only one, *viz.*, **Induline Scarlet**,



seems to possess any technical value.

This is prepared by fusing azo derivatives of ethyl-*p*-toluidine with *α*-naphthylamine.

Latterly, phenanthrenequinone has been utilised for the production of Azine dye-stuffs. In this manner, Flavinduline or **Induline Yellow** is obtained by the condensation of phenanthrenequinone with *o*. amidodiphenylamine. In the literature the following formula is given for this dye-stuff:—



but its accuracy seems open to question, since previous experience teaches that a dye-stuff can only exhibit affinity towards textile fibres provided it contains auxochrome groups, which are lacking in the above formula.

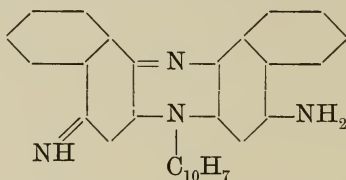
By the action of amines, Flavinduline can be made to yield red to blue dye-stuffs.

ROSINDULINE DYE-STUFFS.

Magdala Red.—This handsome dye-stuff, which gives beautifully fluorescent dyeings on silk, was formerly classed

along with the Safranines, and has only recently been identified as an Induline by O. Fischer and Hepp.

Magdala Red was first obtained by Schiendl (1867) by heating α -amidoazonaphthalene with α -naphthylamine acetate. At present it is prepared by fusing together naphthylenediamine chloride, α -naphthylamine, and amidoazonaphthalene. O. Fischer and Hepp obtained it from amidoazonaphthalene and phenol, and gave it the formula :—



Notwithstanding its high price, it is still used in silk dyeing, though to a small extent, for the production of rose-red shades.

Rosinduline itself was experimentally introduced, as a tannin dye-stuff, by Kalle & Co. Greater importance has, however, been attained by the disulphonic acid of phenyl-rosinduline, the sodium salt of which (Azocarmine) is highly prized in wool and silk dyeing for its great equalising power. It has been partly superseded by Azofuchsine.

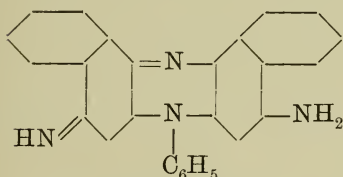
At present Rosinduline is produced in a variety of ways, *e.g.*, by heating anilino- α -naphthylamine with aniline and aniline chloride; by fusing α -nitronaphthalene with aniline and aniline chloride, etc.

An **Ethyl Blue** produced by the Hoechst Farbwerke also seems to be a Rosinduline; it is a basic dye-stuff, noteworthy for the great fastness of its dyeings to washing.

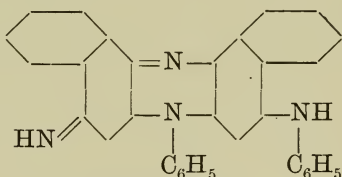
Naphthyl dyes.—Under the names Naphthyl Violet, Naphthyl Blue, and Naphthyl Red, Kalle & Co. put on the market a number of dye-stuffs, which consist of sulphonated Rosindulines, and exhibit certain valuable tinctorial proper-

ties. They are suitable for silk, on which fibre they produce fluorescent dyeings.

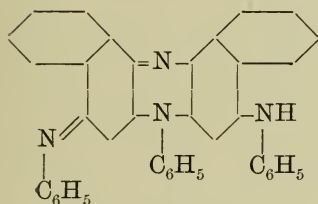
They are produced from various nitrosonaphthol- or -naphthylamine derivatives, as well as by heating benzolazo- α -naphthylamine (phenylated or not) with a naphthylamine chloride and aniline. According to O. Fischer and Hepp, they have the following constitutional formulæ, from which also their near connection with Magdala Red is visible :—



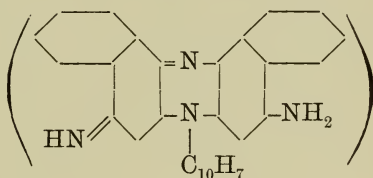
Naphthyl Red.



Naphthyl Violet.



Naphthyl Blue.



Magdala Red.

Naphthyl Violet and Naphthyl Blue are, therefore, phenylated derivatives of Naphthyl Red. Similar substitutions may be also effected by the direct action of amines on Rosindulines, a Tolylosinduline, for instance, having been prepared by acting on phenylosinduline with *o*. toluidine.

Azindone G and R (Kalle & Co.) are indigo-blue tannin dye-stuffs, very closely allied to the naphthyl dyes.

Finally, Kalle & Co. also manufacture sulphonated Rosindones, which give ponceau- to Bordeaux-red fluorescent dyeings on silk. **Rosinduline G** seems to be of this type.

INDULINES AND NIGROSINES.

These dye-stuffs are soluble in spirit or in water, the former class being mostly chlorides and serving, as fast tannin dye-stuffs, in calico printing, and also in the manufacture of lakes and inks. Those soluble in water are generally alkali salts of sulpho acids (obtained by sulphonating insoluble Indulines), and are used in dyeing wool and silk. Nevertheless, there are also Indulines which are naturally soluble in water.

They are all converted by reducing agents into leucobases, which in turn are readily oxidised into the dye-stuffs on exposure to the air. They dissolve in concentrated sulphuric acid and form beautiful blue solutions therein.

As already mentioned, these dye-stuffs are produced from the Induline melt. The "Spirit Indulines" here formed are converted, by further heating with aniline, into valuable blue dye-stuffs (Witt). If they are heated with p. phenylenediamine, an Induline that is soluble in water is formed, the chloride of which compound is put on the market by Dahl & Co., under the name Paraphenylene Blue. It may also be prepared by heating amidoazobenzol with p. phenylenediamine; and a similar product (Oehler's Toluylene Blue) is obtained when the last named component is replaced by p. toluylenediamine.

Indulines soluble in water can also be prepared by modifying the old Induline melt and allowing amidoazobenzol, aniline and aniline chloride to react on each other in a concentrated aqueous solution.

Moreover, Indulines can be produced in a variety of ways, *e.g.*, by the oxidation of aniline; hence they are also formed in the Fuchsine melt; and the Violaniline mentioned in the description of this process (*q.v.*) is an Induline.

The Coupier Fuchsine process (oxidation of aniline

chloride with nitrobenzol) was applied to the preparation of Nigrosines (grey Indulines), from aniline containing toluidine and xyldine, as far back as 1863; iron, copper, or stannous chloride being added to the melt, to produce blue-black dye-stuffs. Coupier obtained his "bleu-noir" by the use of pure aniline. According to Wolff, Nigrosines can also be prepared by oxidising aniline with metallic chlorides, or by heating fuchsine residues with aniline and acetic acid.

Other methods of formation are :—

Heating azobenzol with aniline chloride to 200-230° C. (Städeler) or with p. phenylenediamine and a little sal ammoniac (Fr. Bayer & Co.); in the latter case, water Indulines are formed.

From phenols or quinones and amidoazo bodies, or from oxyazo compounds and aniline.

Amidoazo compounds of the naphthalene series and diamines, containing a tertiary amido group, furnish water Indulines (B. A. S. F.).

The action of paradiamines on certain azo dye-stuffs from (1. 5. and 1. 8.) naphthylenediamines, or on tetrazo compounds of α -naphthol, *e.g.*, $(C_6H_5N=N-)_2 = C_{10}H_5OH$ (O. Hoffmann).

By fusing amidoazobenzol, or finished Indulines, with benzidine chloride; in this event, substantive cotton dye-stuffs are formed (R. Hirsch).

The greyish-blue Nigrosines, which are closely allied to the Indulines, are prepared in a similar manner. According to a proposal made by H. Caro, the dye-stuffs obtained from amines and azo compounds are called Indulines, and those from nitrobenzol or nitrophenols are termed Nigrosines.

Fast Blue R, B, Spirit Induline 3B and 6B, Indigene Printing Blue, etc.—These are the commercial names applied to the chlorides of the various blue products of the Induline melt. Acetine Blue is a solution of Induline in acetine,

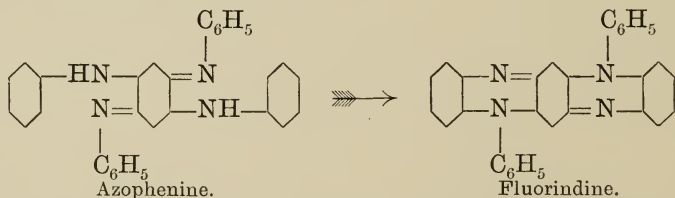
which latter is prepared by the action of acetic acid on glycerine.

The foregoing dye-stuffs are very largely used for the production of dark, fast, indigo blue shades, in calico printing. They are converted, by sulphonation, into soluble acid dye-stuffs, which are sold, in the condition of their sodium salts, under the names Fast Blue R, 3R, Induline 3B, 6B, etc., and are used for dyeing wool and silk.

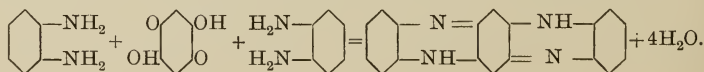
To the blue Indulines also belong Paraphenylene Blue (Dahl), Oehler's Toluylene Blue, and Indamine Blue (M. L. Br.). All these are of small practical importance; but greater value attaches to the Blue Black and Fast Blue Black (a mixture) of the Hoechst Farbwerke.

FLUORINDINES.

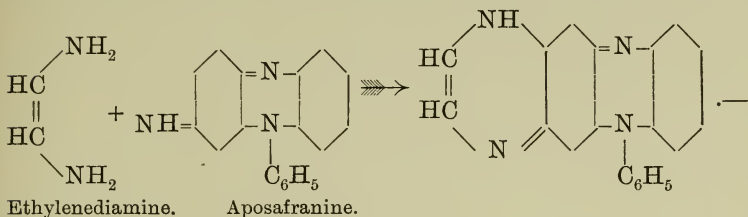
This name is applied to a series of dye-stuffs discovered by H. Caro and Witt. They are prepared by heating Induline bases above the fusing point, and are, therefore, always formed when an Induline melt is treated at high temperature. A characteristic feature of these products is the bright red fluorescence of their solutions. They have recently been investigated by O. Fischer and Hepp, according to whom the Fluorindine originating from azophenine has the following constitution:—



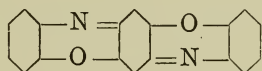
The simplest type of Fluorindine was obtained by the condensation of o. phenylenediamine with dioxyquinone:



Fluorindines are also obtained from o. diamidophenazines and o. diamines, as well as from Aposafranine and diamines:—



Fluorindines, in which the nitrogens are in part replaced by oxygen, and which can, therefore, be called Dioxazines, have also been prepared (from o. amidophenols), *e.g.*, tri-phenindioxazine :



Along with the quinonimide dye-stuffs may, perhaps, be grouped a number of dye-stuffs obtained by the oxidation of various aromatic amido compounds, such as amidodimethylaniline, amidophenols, amidonaphtholsulphonic acids, etc.

A direct cotton dye-stuff, **New Grey** (By.), Methylene Grey (M. L. Br.), etc.,* is obtained by heating nitrosodimethylaniline with water or alcohol.

The name "Ursol" is commercially applied to substances employed to produce brown colorations on furs. The mark P is p. phenylenediamine, D is p. amidophenol, and C is the quinone serving to develop the dyeing (by oxidation).

Aniline Black, which also probably belongs to the quinonimide group, merits more detailed consideration.

The formation of dark green to blue-black substances during the oxidation of aniline salts with chromic acid was observed at an early period by Runge (1834) and Fritzsche

* Other names for this dye-stuff are Metaniline Green (L.), Nigramine (K.), Nigrisine (Soc. An. St. Denis). Cinereine and Noir Phenylène (Soc. St. Denis) are similar.

(1840); and it was subsequently found that the same dye-stuffs could be obtained by the aid of other oxidising agents.

The insoluble dye-stuff prepared in this manner—and also by electrolysis (Goppelsröder)—received the name of Aniline Black.

According to the analyses of Goppelsröder, Kayser, and Nietzki, this substance has the formula $(C_6H_5N)_x$, which recalls the atomic group that plays such a large part in the case of the Indulines, and through whose accumulation in the molecule the simpler Indulines are rendered more complex. This leads to the assumption that Aniline Black is a highly complex Induline, a hypothesis supported by the circumstance that di-p.-diamidodiphenylamine has been obtained by strongly reducing Aniline Black, and that by heating the latter with potassium acid sulphate, a red dye-stuff, similar to Magdala Red, is produced.

When heated with aniline, Aniline Black furnishes a blue dye-stuff; mild reducing agents convert it into a leuco compound; and, when heated for several hours in succession with fuming sulphuric acid, it yields an Aniline-black sulphonic acid (Nietzki) soluble in water.

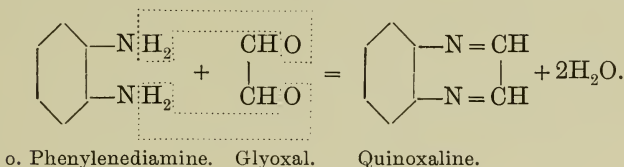
The action of sulphurous acid furnishes a green dye-stuff Emeraldine. This must be considered as a lower stage of oxidation than Aniline Black, since it passes into the latter when oxidised, and appears as an intermediate product in the operations leading to the formation of Aniline Black.

Aniline Black is never sold in the complete state, but has to be produced on the fibre. By reason of the fastness and beauty of its dyeings it forms one of the most important of the dye-stuffs; it is used in cotton dyeing, and latterly has also been employed for dyeing half-silk goods.

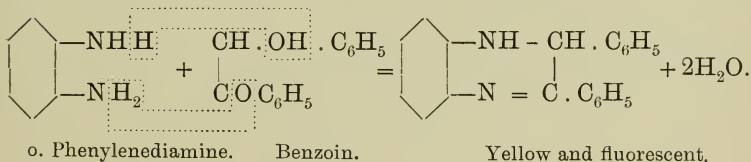
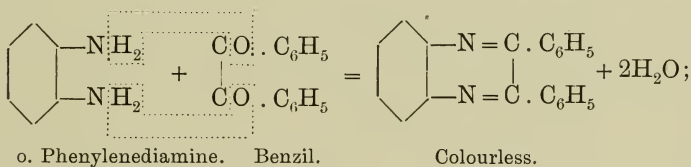
Naphthylamine Violet is a product analogous to Aniline Black, and was obtained by Piria, by the action of oxidising agents on naphthylamine. It has no practical importance.

QUINOXALINES.

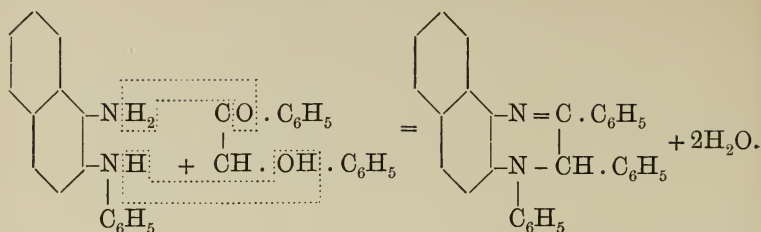
For the time being, the dye-stuffs of this class are interesting solely on account of their resemblance to the Azines. They were discovered by Hinsberg, and are prepared by the condensation of aromatic orthodiamines with diketones or aldehydes. Thus, the typical Quinoxaline is obtained by condensing *o.* phenylenediamine with glyoxal:—



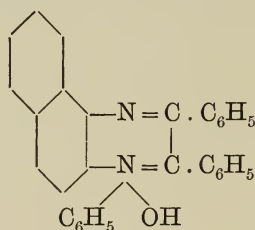
In general the Quinoxalines are colourless bodies; the hydroquinoxalines on the other hand are brightly coloured, *e.g.* :—



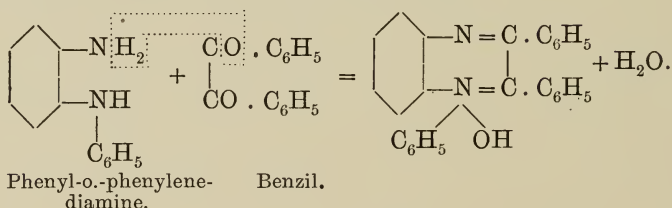
On oxidation, the hydrated quinoxalines pass over into the anhydrous form; the process, however, takes another course when the imide hydrogen is displaced by organic radicles, the products in this event being peculiar “azonium bases,” allied to the Safranines and discovered by Witt:—



When these hydroquinoxalines are oxidised the following azonium base is obtained :—

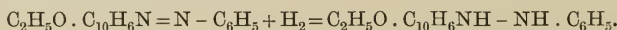


The simplest representative of this class of bodies was discovered by Kehrman and Messinger :—

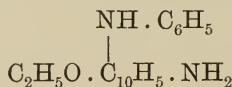


If, in this operation, phenyl-o.-phenylenediamine be replaced by its amido derivatives, azonium bases are obtained which exhibit many similarities with the Safranines.

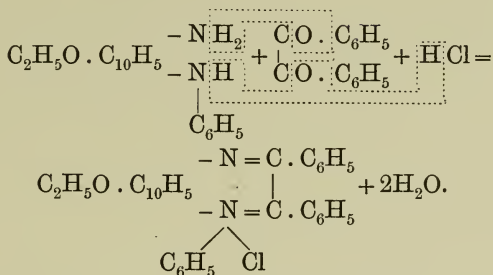
Some azo compounds suffer, on reduction, a peculiar transposition, which can be expressed as the half-completed formation of benzidine. From these substances, Witt has prepared Quinoxalines :



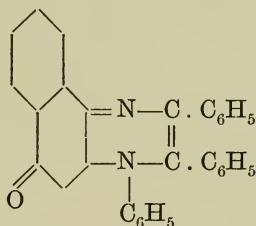
On transposing these hydrazo compounds, there ensues :—



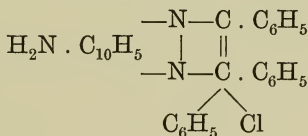
On treating this compound with benzil, in presence of hydrochloric acid, the chloride of an azonium base is obtained :—



If this substance be heated by itself, there ensues a substance similar to Rosindone (by elimination of $\text{C}_2\text{H}_5\text{Cl}$), and capable of dyeing silk red :—



but if heated with ammonia, it furnishes a beautiful rose-red dye-stuff, allied to the Safranines :



INDIGO.

Many plants, especially those belonging to the *Indigofera*, contain a blue colouring matter to which the name of Indigotine or Indigo Blue has been applied. It occurs in

the form of a glucoside called Indican, which on being treated with acids is decomposed into Indigo Blue and dextrose, a kind of sugar.

On treating these plants by a special process of lixiviation a product is recovered which, in addition to its chief constituent, Indigo Blue, contains other dye-stuffs, such as Indigo Red and Indigo Brown, together with Indigo glutin and inorganic matters.

This product, which is only obtained in tropical countries, bears the name "Indigo," and has played a principal part in the dyeing of textile fibres from time immemorial. Indeed even now Indigo is the most important dye-stuff known. This position it owes to its great fastness, a quality in which it is unsurpassed by any other blue dye-stuff.

At present we shall deal merely with the chemical aspect of Indigo Blue, the details of its preparation, etc., being described under "Natural Dye-stuffs".

For the synthetic preparation of Indigo Blue and the elucidation of its constitution we are indebted almost exclusively to the renowned labours of Ad. Baeyer on this subject. Previous to his researches the facts relating to the constitution of Indigo Blue were few in number, in so far as the same were of any use to investigators. Thus it was known that Indigo is converted into Isatin by oxidation; that it furnishes aniline when distilled with potash; anthranilic acid when fused with the same alkali; and nitrosalicylic and picric acids when treated with concentrated nitric acid.

From the fact that simple aromatic compounds are furnished when the molecule of Indigo Blue is strongly attacked, the conclusion could be drawn that this molecule must contain at least one benzol nucleus. Moreover, the formation of anthranilic acid (o. amidobenzoic acid) indicated

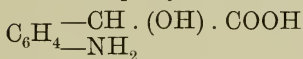
that this benzol nucleus must be present in the form of the atomic group $\text{C}_6\text{H}_4 - \text{C} \equiv \text{N} =$.

Baeyer first attempted to reconvert Isatin, the oxidation product from Indigo Blue, into the dye-stuff itself, by reversing the chemical process, *i.e.*, by reduction. Though at the outset this proved unsuccessful, he nevertheless came by this means to other substances, such as Oxindole, Dioxindole, and subsequently to Indole itself, the study of which greatly facilitated the identification of the constitution of Indigo Blue.

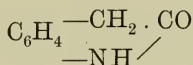
Oxindole proved to be the internal anhydride of *o.* amidophenylacetic acid, and Dioxindole that of *o.* amidomandelic acid :



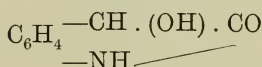
o. Amidophenylacetic acid.



o. Amidomandelic acid.



Oxindole.



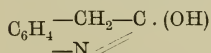
Dioxindole.

Subsequently,* the Indole, $\text{C}_6\text{H}_4 - \begin{array}{c} \text{—CH} = \text{CH} \\ \text{—NH} \end{array} \diagup$, forming the basis of these two compounds, was also discovered.

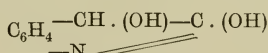
That, as was assumed by Baeyer, Indole is closely connected with Indigo Blue was afterwards proved by the formation of Indigo Blue during the treatment of Indole with ozone (Nietzki, 1875).

If the formula given above for Indole be correct, it follows

* Other reasons, such as the formation of Oxindole and Dioxindole from Isatin, speak in favour of a somewhat different constitution of this substance, as may be expressed in the following formulæ :—



Oxindole.



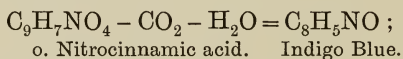
Dioxindole.

that the substance taken as the primary material for its synthesis must contain the atomic complex $\text{C}_6\text{H}_4 - \begin{smallmatrix} \text{CH} = \text{CH} \\ \text{N} = \end{smallmatrix}$.

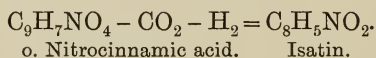
Such a substance was found by Baeyer and Emmerling in orthonitrocinnamic acid, $\text{C}_6\text{H}_4 - \begin{smallmatrix} \text{CH} = \text{CH} \\ \text{NO}_2 \end{smallmatrix} \cdot \text{COOH}$, which they actually succeeded in converting into Indole in 1869 by fusing it with potash and iron filings. The potash in this reaction acts as an eliminator of carbon, the iron as a deoxidising agent.

Starting with the conviction that Indole must be very closely related to Indigo Blue, Baeyer then endeavoured to arrive at this latter by means of the compound from which he had prepared Indole, namely, o. nitrocinnamic acid.

On comparing the empirical formula of Indigo Blue with that of the acid in question, they really seem to be very closely connected:—



and o. nitrocinnamic acid appears also to be nearly allied to Isatin:—



The relationship is, however, not of a very simple character, since, in the first place, in accordance with the vapour density found by Sommaruga, Indigo Blue has the doubled formula ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$), and secondly, the conversion expressed by the above equation cannot be effected by the corresponding means, *e.g.*, by treatment with concentrated sulphuric acid.

Baeyer was aware that the carbon dioxide could be easily eliminated from o. nitrocinnamic acid. Consequently, all that was necessary was to remove from the acid in question

Blue by a simultaneous slight reduction, effected by the addition of grape sugar.

Indigo Blue, or Indigotin, therefore, is formed when *o.* nitrophenylpropionic acid is heated with alkali and grape sugar.

This justly admired synthesis of Indigo Blue, which was effected by Baeyer* in 1880, at first led to very sanguine hopes with regard to its practical consequences, and it was believed that natural Indigo would very soon be displaced by the artificial product, just as madder had been superseded by Alizarine.

As a matter of fact, artificial Indigo Blue possesses certain valuable advantages over the natural article, for calico printing in particular, inasmuch as the final stage of the Baeyer synthetic process—the conversion of *o.* nitrophenylpropionic acid into Indigo Blue—can be performed on the fibre. In this connection the most suitable reducing agent has proved to be sodium xanthogenate, and borax the best alkali.

In this propionic acid printing process,† *o.* nitrophenylpropionic acid in paste form (B. A. S. F.) is printed on the fibre along with sodium xanthogenate, borax and starch thickening, the reaction (removal of carbon dioxide, and reduction) being then effected by hanging the fabric in a warm chamber.

On account of its numerous defects, however, this blue is not very extensively employed in practice. The main reason why this artificial Indigo could not compete with the natural article was to be sought in the high price of the former, this being the consequence of the poor yield furnished by the synthetical process. When cinnamic acid is nitrated,

* *Berl. Ber.*, **13**, p. 2254.

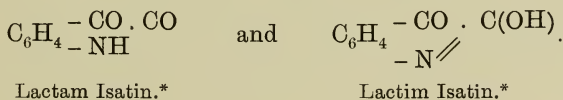
† *o.* Nitrophenylpropionic acid is also termed propionic acid for short.

only a comparatively small quantity of the orthonitro derivative—which alone is suitable for the production of Indigo—is formed in addition to p. nitrocinnamic acid; and even though the nitration of cinnamic ester furnishes 70 per cent. of the acid in the form of the orthonitro derivative, this yield is still too small to render the operation profitable. Finally, also, the conversion of o. nitrophenylpropionic acid into Indigo Blue is by no means a smooth process, a portion being always changed into Isatin.

Apart from Indole the study of two other bodies of the Indigo group, *viz.*, Isatin and Indoxyl, led Baeyer to his elucidation of the constitution of Indigo Blue.

Isatin has an acid character, and gives metallic compounds, which by absorbing water readily pass over into salts of the so-called isatinic acid. It was identified as o. amidophenylglyoxylic acid, $C_6H_4 - \underset{NH_2}{CO} \cdot COOH^{(1)}$; and Isatin must be regarded as its internal anhydride, $C_6H_4 - \underset{NH}{\overset{-CH \cdot CO}{\diagup}}$.

Other facts favour the hypothesis that Isatin must exist in two modifications, only one of which is stable in the free state. Such forms as are incapable of existing in that state are termed “labile” or “pseudo” forms by Baeyer, who gives the following as the two formulæ of Isatin:—



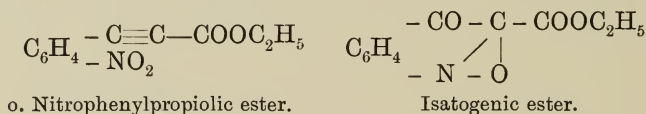
As already mentioned, the first attempts to convert Isatin into Indigo Blue by reduction were not successful. The reagents then used did not merely deoxidise, but also intro-

* These names were recently proposed by Ad. Baeyer to replace those formerly in use, *viz.*, pseudoisatin and Isatin (*Berl. Ber.*, **33**, Sonderheft, p. lxx.).

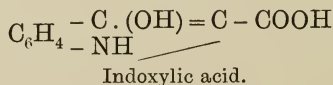
duced hydrogen. As soon, however, as Baeyer resorted to reducing agents unattended with this latter defect (phosphorous trichloride, chloracetyl and a little phosphorus) he obtained the desired result.

This conversion of Isatin into Indigo Blue must be regarded as the first synthesis of the latter, as Baeyer also very soon after (1878) succeeded in preparing Isatin from Oxindole, by synthesis. On account of the extremely low yield obtained, the earlier reported formation of Indigo Blue from Indole (Nencki, 1875) can only count as indicating the method of formation.

Finally, with regard to Indoxyl, the third compound contributing—and most of all—to the elucidation of the constitution of Indigo Blue, this substance was synthetically prepared by Baeyer in the following manner.* The action of concentrated sulphonic acid on the ethyl ester of *o*. nitrophenylpropionic acid is to convert the latter into an isomeric compound by molecular transposition. This product is the ethyl ester of an acid which is readily convertible into Isatin, and has, therefore, been named isatogenic acid :

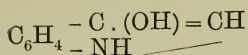


By the action of reducing agents the isatogenic ester is converted into indoxylic ester, the latter, on saponification, then furnishing free indoxylic acid :

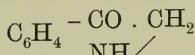


When this acid is heated to fusing point, it liberates carbon dioxide, and passes over into Indoxyl, which, like Isatin, may exist in two modifications :—

* Discovered by Baumann and Tiemann (*Berl. Ber.*, **12**, p. 1098).

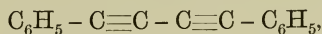


Enolindoxyl.



Ketoindoxyl.

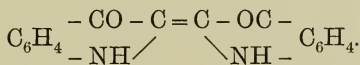
The particular ease with which Indoxyl can be oxidised into Indigo Blue, led Baeyer to decisively assume that a combination of two molecules of Indoxyl occurs in this transition. Now, in order to bring this assumption into accord with the formation of Indigo Blue from o. nitrophenylpropionic acid, it is necessary to look upon Indigo Blue as a derivative of a diphenyldiacetylene:



the accuracy of which hypothesis has been demonstrated by the synthetic conversion of o. dinitrodiphenyldiacetylene into Indigo Blue.

Many reasons favour the belief that the two nitrogen atoms in Indigo Blue are contained as imide groups, and that the two oxygen atoms are attached to the two carbon atoms nearest to the benzol nucleus.

Consequently, Indigo Blue has the following constitutional formula:—

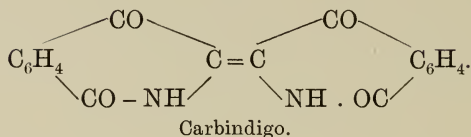
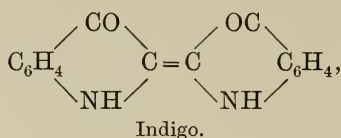


Indigo Blue.

Just as Indoxyl, $\text{C}_6\text{H}_4 - \text{C} \begin{array}{l} \text{-(OH)=CH} \\ \text{---NH} \end{array}$, is converted by oxidation

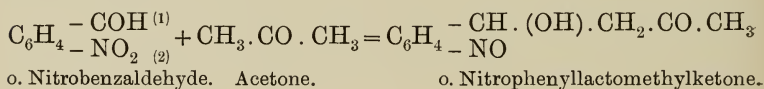
into Indigo Blue, so an analogous compound, 4. oxyisocarbostryl, $\text{C}_6\text{H}_4 - \text{C} \begin{array}{l} \text{-(OH)=CH} \\ \text{---CO.NH} \end{array}$, on oxidation furnishes a red

substance, to which S. Gabriel and J. Colmann gave the name "Carbindigo," and which is entirely analogous to Indigo in composition:—

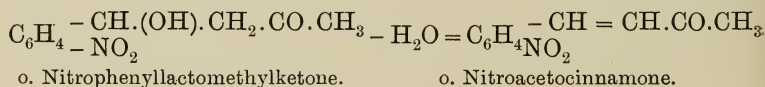


It also behaves like Indigo under oxidation and reduction.

Synthesis of Indigo from o. nitrobenzaldehyde (Baeyer and Drewson). The condensation of o. nitrobenzaldehyde with acetone furnishes in the first place o. nitrophenyllactomethylketone :



which, by elimination of water, is converted into o. nitroacetocinnamone :

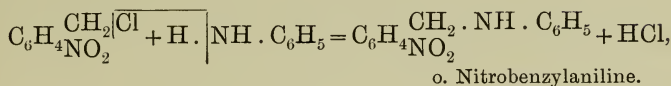


This last-named product is readily converted, by caustic alkalis, into Indigo Blue.

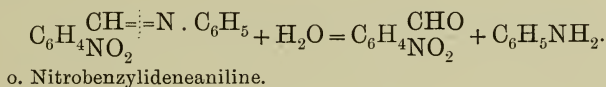
This long-known synthesis has latterly been utilised industrially, the aforesaid intermediate product, o. nitrophenyllactomethylketone, being sold by Kalle & Co. under the name "Indigo salt," and used for producing Indigo Blue on the fibre in calico printing.

It seems of late as though the preparation of Indigo from o. nitrobenzaldehyde were about to attain high technical importance, the Hoechst Farbwerke having succeeded in finding a method for easily converting o. nitrotoluol into o. nitrobenzaldehyde. With this object, the first-named

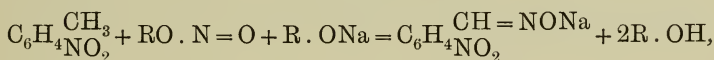
compound is chlorinated in the lateral chain, then united with aniline to an anilido derivative :—



which is oxidised into a benzylidene compound, and the latter finally split up, by acids, into o. nitrobenzaldehyde and aniline :



According to a second process of the same firm, o. nitro-toluol is combined with amyl nitrite, in presence of sodium alcoholate, to form o. nitrobenzaldoxime :



from which o. nitrobenzaldehyde can be easily recovered by known methods.

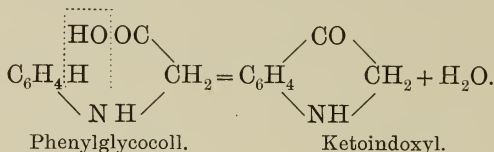
Another method for the direct conversion of o. nitro-toluol into the corresponding aldehyde, consists in oxidising the former with manganese peroxide and sulphuric acid (Soc. des Usines du Rhone, Gilliard, Monnet & Cartier), for which a licence has been acquired by the Hoechst Farbwerke. This last firm has recently put on the market a crystalline Indigo prepared by this method.

At present this synthesis is only of restricted technical importance, and it would be impossible, owing to the insufficient available quantity of toluol, to replace by this method all the natural Indigo consumed throughout the world.

K. Heumann's Synthesis of Indigo Blue.—Whereas formerly all the syntheses of Indigo employed bi-substitution products of the orthobenzol series as raw material, mono-

substitution products of benzol have latterly been used for this purpose.

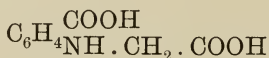
Thus, phenylglycocoll, $C_6H_5NH.CH_2COOH$, when fused with potash, furnishes ketoindoxyl, which is readily converted into Indigo Blue by atmospheric oxidation:—



Derivatives of phenylglycocoll are also capable of this reaction, and furnish substituted Indigo Blues, which are greener than Indigo Blue itself, the more so when the phenylglycocoll employed was not substituted in the nucleus.

Thus, for instance, the compound $C_6H_5N-\overset{\diagup}{CH_3}CH_2.COOH$, on being fused with potash, gives a very greenish blue, which, when treated with fuming sulphuric acid, furnishes a green-dyeing sulphonic acid (B. A. S. F.).

Whilst the synthesis of Indigo from phenylglycocoll possesses a merely theoretical interest owing to the low yield obtainable, high technical importance now attaches to the preparation of this dye-stuff from orthocarbophenylglycinic acid:

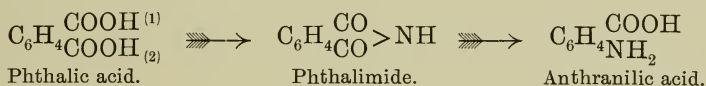


For the last twenty years the Badische Anilin- und Soda-fabrik has ceaselessly endeavoured to prepare synthetic Indigo at a price capable of competing with the natural article, which result it has now succeeded in attaining by the process in question.

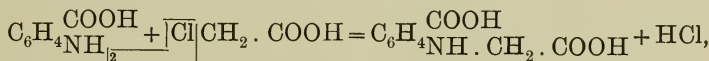
Under the name "Indigorein" a synthetic Indigo, consisting of almost chemically pure Indigo, and already largely used in dyeing and printing, has been placed on the market

by the above firm ever since July, 1897. This product, which is usually in the form of a 20 per cent. paste, costs about 1s. 3d. per lb.; and a still more finely divided quality is sold as "Indigo S".*

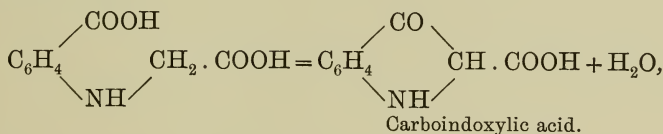
The primary material for the preparation is naphthalene, which is available in any desired quantity, but which has latterly almost doubled in value. By heating naphthalene with strong sulphuric acid in presence of mercury, phthalic acid is obtained in the cheapest manner imaginable. This is next converted into phthalimide, which can then be readily transformed with chlorine and caustic soda into anthranilic acid:



Anthranilic acid and chloracetic acid furnish orthocarbophenylglycinic acid:



which is finally converted into Indigo by heating with caustic soda. The first product of this reaction is carboindoxyl acid:



which is changed into Indigo when the alkaline solution is treated with a current of air.

If orthocarbophenylglycinic acid be heated with caustic alkalis in presence of air, Isatin is produced in considerable amount. †

* This product is obtained by dissolving Indigorein in concentrated sulphuric acid, and reprecipitating with water.

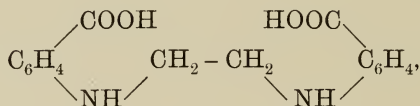
† This also affords the possibility of producing Indigo Red on a technical scale.

Carboindoxylic acid has long been sold in the form of an unstable greyish-green powder under the name Indophor for the production of Indigo on the fibre in calico printing.

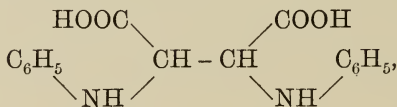
The conversion of orthocarbophenylglycinic acid into an indoxyl derivative can be effected with particular ease by heating its salts with acetic anhydride, a diacetylindoxyl being formed, partly even below 110° C. (By.). In the same manner neutral esters of orthocarbophenylglycinic acid, when heated with sodium alcoholate, readily furnish indoxylic ester.

As was discovered by Fr. Bayer & Co., the readiest reaction is given by the neutral esters of acetylated orthocarbophenylglycinic acid, which are converted at water-bath temperature into Indigo leuco compounds when warmed with aqueous or solid alkalis.

It is an interesting fact that neither ethylenedianthranilic acid :



(Fraenkel and Spiro), nor dianilidosuccinic acid (Vorlaender) :

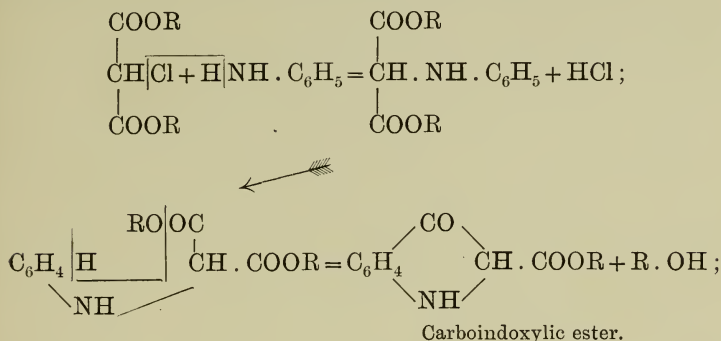


is suitable for the preparation of Indigo, though an investigation of their constitutional formulæ would indicate the contrary. When heated with potash and subsequently oxidised, the first named gives only a small percentage of Indigo, the other none at all.

Of other synthetic methods of preparing Indigo mention may be made of the following :—

R. Blank's Indigo Synthesis.—Chloromalonic ester is con-

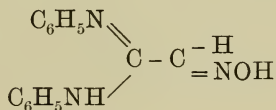
densed with aniline to an anilide, which, when heated, gives off alcohol and is converted into carboindoxylie ester :



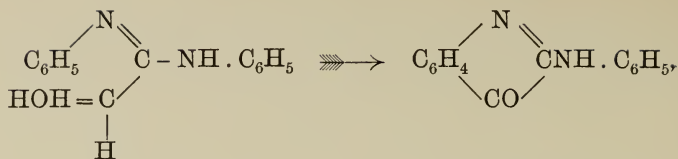
which can readily be converted into Indigo by saponification and oxidation. The first reaction, *i.e.*, the formation of the indoxyl derivative, goes on with particular ease and smoothness when naphthalene derivatives are used, *e.g.*, when a naphthylamine is substituted for aniline. When aniline is taken, the reaction progresses all right on the small scale; but on the large scale so many bye-products are formed as to render the technical utilisation of the reaction impossible.

Sandmeyer's Indigo Synthesis.—

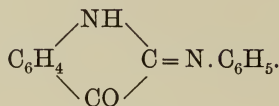
Chloral ($\text{CCl}_3 \cdot \text{CHO}$) combines with hydroxylamine to form trichloraldoxime ($\text{CCl}_3 \cdot \text{C} = \text{NOH}$); on treating this with aniline, all three chlorine atoms are displaced by aniline radicles, and an isonitrosoethylenediphenylamidine,



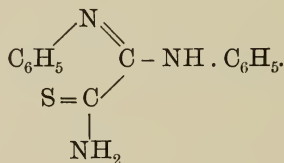
is produced. When this product is warmed with concentrated sulphuric acid, it liberates ammonia, and is converted into α -isatinanilide :

 α -Isatinanilide.

or

 α -Isatinanilide.

This highly noteworthy reaction proceeds in a still easier, and almost quantitative manner, when thiamide* is employed:—



The resulting isatinanilide can be readily converted into isatin or Indigo.

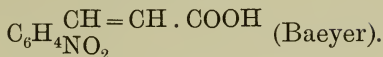
REVIEW OF THE SYNTHESSES AND METHODS OF PRODUCING INDIGO.

The syntheses or methods of formation of Indigo may be arranged in three classes:—

1. Syntheses from such aromatic compounds as contain a nitro group in the ortho position to a carbon chain; to this class belong the syntheses:—

* This is obtained by combining hydrocyanic acid and carbodiphenyl-imide to produce hydrocyanicarbodiphenylimide, which is then treated with yellow ammonium sulphide, the result being an addition of 1 molecule of H_2S .

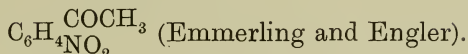
From o. nitrocinnamic acid,



From o. nitrobenzaldehyde,



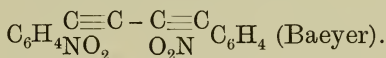
From o. nitroacetophenone,



From o. nitrophenylpyroracemic acid,



From o. dinitrodiphenyldiacetylene,



2. Syntheses from amido compounds containing the necessary lateral carbon chain either in the amido group, or in the benzol nucleus, in the ortho position thereto; to this class belong the syntheses:—

From phenylglycocoll, $\text{C}_6\text{H}_5\text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$ (Heumann).

From orthocarbophenylglycinic acid,



From bromacetanilide, $\text{C}_6\text{H}_5\text{NH} \cdot \text{COCH}_2\text{Br}$ (Flimm).

From anilidomalonic ester,



3. Syntheses from compounds, like isatin and indole, already containing the ring $\text{C}_6\text{H}_4 \begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{N} \end{array}$ characteristic of

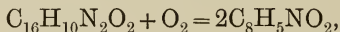
Indigo.

Indigo Blue or Indigotin is a substance insoluble in ordinary solvents, exhibits neither acid nor basic properties, and consequently cannot be taken up, in its ordinary form, by textile fibres.

An important feature of this body is its behaviour on reduction or oxidation. Under the influence of reducing agents it changes into the colourless Indigo White, which is of acid character, and is readily soluble in alkalis. Since it also exhibits an affinity for textile fibres, and is readily reconverted, by oxidation, into the insoluble Indigo Blue, it is employed for dyeing goods in the so-called Indigo vat. This is nothing more than an alkaline solution of Indigo White, obtained by treating Indigo with a cheap reducing agent. When a fabric is impregnated with such a solution, and is then exposed to the air, the Indigo White is oxidised into Indigo Blue, which is deposited firmly on the fibres, and imparts thereto a fast blue coloration.

This ready reduction and reoxidation is utilised in the preparation of pure Indigo from the commercial quality, and also forms the principle of a number of methods that have been proposed for determining the value of Indigo.

Oxidising agents convert Indigo Blue into isatin :



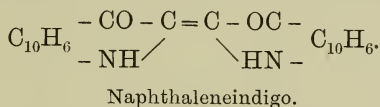
a reaction on which is based the white discharging of goods dyed with Indigo, as well as various testing methods, the most important of which is that of Mohr (oxidation with potassium permanganate).

Of the derivatives of Indigo, only one is of any interest, namely the disulphonic acid obtained by the action of concentrated sulphuric acid on Indigo, and the sodium salt of which is commercially known as Indigocarmine. As an acid dye-stuff the sole employment of Indigocarmine is in

the dyeing of silk and wool, in which operation it formerly played an important part. Its dyeings are bright, but very fugitive, and it is now seldom used, suitable substitutes having been found in certain newer dye-stuffs, such as Patent Blue, Fast Green, Acid Green, etc.

Indigosulphonic acid has been synthetically prepared by B. Heymann by treating phenylglycocoll with sulphuric acid rich in anhydride. The first product is a kind of leuco compound, which is transformed into indigodisulphonic acid on diluting the solution with ordinary sulphuric acid.

Mention may finally be made of the preparation of an α - and β -naphthaleneindigo from α - and β -naphthylglycocoll—on the same lines as the Heumann synthesis—by H. Wichelhaus. These compounds are green dye-stuffs and their constitution corresponds to that of ordinary Indigo Blue:



They can be obtained, with very good yield, by the Blank synthesis, but apparently have no technical value.

Bibliography.

For full information with regard to the synthesis and manufacture of Indigo, reference may be made to two recent interesting papers by Ad. Baeyer and H. Brunk (*Berl. Ber.*, 33, Sonderheft).

The labours of Baeyer have been most fully described by R. Meyer in Bolley's *Handbuch der chemischen Technologie*; and a more condensed report will be found in the present author's pamphlet on Indigo (Fr. Deuticke, Leipzig).

DYE-STUFFS OF UNKNOWN CONSTITUTION.

Under this title will be given a description of certain dye-stuffs, which exhibit no similarity with any of those already dealt with, and are of unknown constitution.

Murexide.—This dye-stuff is the acid ammonia salt of purpuric acid, which latter is unknown in the free state. The dye-stuff is formed when a solution of uric acid is evaporated with concentrated sulphuric acid, and the residue treated with ammonia. It dissolves to a beautiful purple-red solution in water, the solution being turned to blue-violet by an excess of alkali, and decolorised by acids.

Murexide and picric acid are the oldest dye-stuffs known. Between 1850 and 1860, Murexide was prepared in large quantities, from the uric acid of guano, especially by Robert Rumney (up to about 2 cwt. per diem), and was largely used ; but it has not been on the market since 1864.

Murexide was used *per se*, but to a larger extent in the form of free acid, which latter was sold as Purple Carmine. Mercury and lead salts were generally used as the fixing agents, red colour lakes being produced ; zinc mordants gave yellow dyeings, copper mordants gave yellowish-greens.

Fabrics of animal fibre were mostly mordanted beforehand with mercury chloride and oxalic acid, and then treated in the dye-bath ; or else the procedure was reversed, the goods being first impregnated with the dye solution and then mordanted. Single-bath dyeing was also practised.

In the case of cottons, lead oxide was first precipitated on the fibre, and the goods then dyed.

Murexide was especially used in calico printing, the pieces being generally printed with a salt of mercury or lead, and afterwards fixed and dyed.

Canarine ($C_3N_3S_3H?$) is a sulphur dye-stuff obtained by

treating potassium thiocyanate with potassium chlorate and hydrochloric acid.* Its tinctorial power is slight, but it has the property of dyeing cotton direct in an alkaline bath, the dyeings being very fast except to light. Its production, however, has been discontinued. Recently the manufacture of a similar product was patented by Goldberg, Siepermann and Flemming, the process consisting in reacting with gaseous chlorine on potassium thiocyanate at temperatures below 200° C. The same dye-stuff is said to be also furnished by the action of sulphur trioxide on potassium thiocyanate.

SULPHUR OR SULPHINE DYE-STUFFS. †

Under this name there has been on the market for several years a number of dye-stuffs, which, owing to their property of dyeing cotton direct and very fast, possess a high practical value, and for the moment form the chief object of interest to the practical colour chemist. Their behaviour in dyeing ranks them between the dye-salts and the vat dyes, since, while they act as substantive cotton dyes, the true dyeing is mostly obtained by subsequent oxidation.

At present, all shades of colour, except red and yellow, are represented in this group of dye-stuffs, the blacks and browns being the most important.

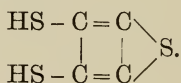
Both from the method of production and behaviour during dyeing, their composition may be assumed as highly varied, though their true constitution is still unknown. Meanwhile they may be classed together in a group possessing a thiophenol character which influences their solubility in alkali sulphides.

* A new method of production was described by Pawlewski (*Berl. Ber.*, 1900, p. 3164).

† See also an article by Dr. Jaeck on this subject in the *Revue Générale des Matières Colorantes*, 1899, Nos. 33 and 34.

Cachou de Laval may be regarded as the forerunner of the sulphine dye-stuffs. The product known by this name was first prepared by Croissant and Bretonnière, by fusing sawdust, bran, etc., with sodium sulphide. Like Canarine, it produces a direct yellow dye on cotton in an alkaline bath, but differs from this latter dye-stuff, inasmuch as the dyeings are greenish at first, and only become the proper (brown) colour after oxidation in the air. The fastness to which this dye-stuff owes its popularity as a cheap fast bottoming for cottons is produced by an after-treatment with metallic salts (iron, chrome, copper).

The first scientific investigation of Cachou de Laval was undertaken in 1896 by Richardson and Akroyd.* The specially purified product examined by these workers gave, on analysis, figures from which the formula $C_{33}H_{16}S_{26}O$ was deduced. By eliminating the oxygen from this formula, we come to the simplified symbol $H_2C_4S_3$, which Richardson and Akroyd arranged as follows:—



According to this view, Cachou de Laval would be a thiophene derivative.

The important **Sulphine dye-stuffs** were not discovered until twenty years later than Cachou de Laval. The chief method of preparation consists in treating a variety of—mostly nitrogenous—aromatic compounds with sulphur and alkali sulphide, by fusion at temperatures between 180 and 250° C.

This method was discovered by Vidal,† who based on the method employed for producing Cachou de Laval, and applied the same to o. and p. dioxybenzol, dioxynaphthal-

* *Journ. Soc. Chem. Ind.*, 1896, p. 328.

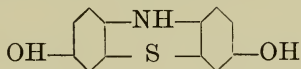
† French Patent, 231,118, 1st July, 1893.

one, and α -naphthoquinone, nitrogen being introduced into the melt in the form of ammonia or amines of the fatty series.

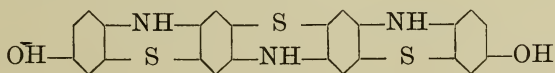
The first of these Vidal dye-stuffs differed from Cachou de Laval, inasmuch as their dyeings turned black, instead of brown, on oxidation. This difference was caused by their nitrogen content, since without this latter in the sulphur melt the method yielded brown dye-stuffs exclusively. The importance of the para derivatives was also apparent in these early patents.

Subsequently, Vidal made direct use of nitrogenous components, such as the diamines and amidophenols of benzol, or azo combinations furnishing these substances when split up by reduction. The **Vidal Black** obtained from p. amido-phenol possesses a particular interest, since it was the means of instigating the technical investigation of this branch of the dye-stuff industry.

To its discoverer we are also indebted for the first scientific researches on these dye-stuffs. Vidal found that Bernsthen's dioxythiodiphenylamine,



appears as an intermediate product of the fusion of p. amido-phenol with sulphur. It is formed by the coalescence of two molecules of p. amidophenol, with elimination of ammonia, and Vidal assumes that this thiodiphenylamine derivative is converted, by the concurrent action of ammonia and sulphur, into a p. dioxytetraphentritiazine,



which compound is said to form the chief constituent of Vidal Black.

This, in any case very hypothetical, conception of the dye-stuff in question as an oxythiophenylamine derivative, has much in its favour, since it explains the solubility of the dye-stuff in alkalis, and its property of forming a kind of vat process, as will be seen also in the case of a simple representative of this class of substances, *p.* oxythiodiphenylamine.

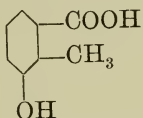
Vidal also examined meta derivatives (dioxy-, amidobenzols, etc.) in the sulphur melt, and equally obtained brown and black Sulphine dye-stuffs. The employment of primary materials containing more chromophore or auxochrome groups, such as diamido- and dinitro-phenols, or naphthols, brought him to dye-stuffs differing from the foregoing by a greater affinity for cotton and greater rapidity of oxidation when dyed.

There are a number of other patents, the chief of which will now be mentioned :—

The so-called **Thiocatechins** (Soc. Anon. St. Denis) are prepared from partly acetylated diamines; a Fast Black (B.) has been obtained from 1. 5. and 1. 8. dinitronaphthalene; Fr. Bayer & Co. employ for the sulphur melt, sulpho acids of amines, phenols, amidophenols, carbo acids of amines and phenols, and, finally, also the unsubstituted phenols and naphthols, the interesting observation being recorded that the dye-stuffs from the homologues of phenol have a greater affinity for cotton than those from the simple phenols, and that, therefore, in this case, contrary to expectation, an important part is played by the CH_3 group. The Badische Anilin- und Sodafabrik has obtained from 1. 5. dinitroanthraquinone, a black dye-stuff, which, while exhibiting the tinctorial properties of a Sulphine dye-stuff, is, according to Jaecks, to be classed with the Alizarine Black group of dye-stuffs. The dye-stuff known as Anthraquinone Black (B.) differs from the foregoing. In addition, dioxy- and

amidooxynaphthalene sulphonic acids have been submitted to the sulphur melt; under this treatment, the 1. 8. derivatives give blue to black dye-stuffs, whilst 1. 8. chloronaphthol sulphonic acids and their azo compounds furnish green dye-stuffs. Violet dye-stuffs have been obtained from nitroso-dioxynaphthalene sulphonic acids; and Sulphine dye-stuffs have also been prepared from Indamines, Indophenols (Im-medial Pure Blue), and mixtures of amidophenols with a variety of substances, as well as from compounds containing neither amido- nor hydroxyl groups (*e.g.*, anthraquinone sulphonic acids), and from such naphthalene polysulphonic acids as contain two sulpho groups in the meta position.

In the latter case a carbocresolic acid,



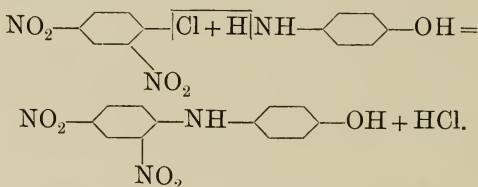
is probably formed as an intermediate product.

As may be gathered from the above sketch, the most heterogeneous substances are employed for the formation of dye-stuffs under this valuable new method. The truly empirical attempts in this branch vividly recall the early days of the aniline dye-stuff industry.

The first important advance in this branch was made by the use of diphenylamine derivatives. It had already been recognised by Vidal that the Sulphine dye-stuffs are derived from diphenylamine, and it was therefore to be expected that the direct employment of a diphenylamine derivative would facilitate the progress of the sulphur melt. This has been found to be the case, the resulting advantage consisting in the fact that the melt can be carried on at a far lower temperature (140 to 180° C.) than in the Vidal method, the consequence being that a much purer product is obtained. The credit for this advance is due to Cassella & Co., who

made a particularly happy choice in selecting a metadinitro-diphenylamine derivative. The consequence was that a large number of diphenylamine derivatives—most of which had first to be sought for—were subjected to the sulphur melt treatment by a large number of workers.

The diphenylamine derivatives are produced by heating an amine in aqueous or alcoholic solution with a chloro-derivative (substituted in the nucleus), in presence of a neutralising agent, such as sodium acetate, for combining the liberated acid, *e.g.* :—



The resulting p. oxy-o'. p'.-dinitrodiphenylamine furnishes in the sulphur melt the valuable **Immedial Black** (Cassella), which by oxidation on the fibre is converted into the equally valuable **Immedial Blue**.

The excellent properties of **Immedial Black** led to the launching of a large number of patents, in which the most widely divergent diphenylamine derivatives—mostly produced by a variation of the amine—are applied to the preparation of Sulphine dye-stuffs. In place of the p. amidophenol used in the foregoing equation, use is made of nitro-p.-phenylenediamine, dimethylparaphenylenediamine,* p. phenylenediamine sulphonic acid, metanilic acid, sulphanilic acid, o. amidophenol, o. amidophenolsulphonic acid, 1. 3. 4. diamidophenol, picraminic acid, o. amidosalicylic acid, etc., etc.

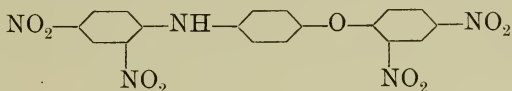
* The diphenylamine derivative from dinitrochlorbenzol and dimethyl-p.-phenylenediamine, $\text{O}_2\text{N---}\langle\text{C}_6\text{H}_3\text{NO}_2\rangle\text{---NH---}\langle\text{C}_6\text{H}_4\text{N(CH}_3)_2\rangle$, furnishes an olive-

green dye-stuff under the sulphur melt treatment.

Dinitrochlorbenzol may be replaced by nitrochlorosulphonic acid, carbonitrochloric acid, etc.

Sometimes also the diphenylamine derivative is nitrated or sulphonated and then put through the sulphur melt process.

Frequently also the above-named diphenyl derivatives can be condensed with a second molecule of dinitrochlorbenzol in alkaline solution, the following compound being formed when the base of Immedial Black is used:—



All the Sulphine dye-stuffs hitherto known are produced by fusion with sulphur, with or without alkali sulphides. There are, however, others of the same class that are obtained in a different manner.

Mention must first be made of a process which is apparently based on the new Methylene Blue method, and consisting in the use of thiosulphate, which, when boiled with various substances in acid solution (nitrosophenol, quinonechlorimides, etc.), furnishes Sulphine dyes either direct (*e.g.*, Clayton Black) or, after fusing with sulphur (diamidophenols, etc.). Dinitronaphthalene (1. 5. and 1. 8.) gives Sulphine dyes, by reduction in aqueous solution with sodium sulphide, and boiling the product with caustic soda (Fast Black BS of the B. A. S. F.). Verde Italiano (Lepetit, Dollfuss & Gansser) is obtained by adding copper to the sulphur melt. L. Cassella & Co. heat o. and p. amidophenol with sulphur chloride to 70° C., afterwards increasing the temperature to 180-200° C. The Clayton Black of the Clayton Aniline Co. is obtained by treating nitrosophenol with acid solutions of thiosulphates. A number of blue and black dye-stuffs, which from their tinctorial properties must be classed with the Sulphine dyes, are prepared by heating p. amidophenol and

sulphanilic acid without any further addition (Ger. Pat., 104,105), the colour depending on the temperature employed. Finally certain new dye-stuffs of this group have been prepared by heating finished Sulphine dyes with caustic alkali alcohol, etc.

The commercial Sulphine dyes comprise: Vidal Black, Immedial Black (C.), Katigene Black (By.), Fast Black (B.), Anthraquinone Black (B.), Sulphaniline Black (K.), Sulphur Black (Act.), Clayton Black (Cl.), Eclipse Black (Gg.), Immedial Blue (C.), Immedial Pure Blue (C.), Cryogene Blue (B.), Melanogene Blue (M. L. Br.), Katigene Green (By.), Verde Italiano (Lepetit, Dollfuss & Gansser), Thiocatechine (Soc. St. Denis), Immedial Brown (C.), Katigene Brown (By.), Sulphogene S (L.), Cryogene Brown (B.), Sulphaniline Brown (K.) and the Pyrogene dyes (Ges. Chem. Ind. Basle).

DEVELOPMENT OF THE ARTIFICIAL DYE-STUFF INDUSTRY.

The earliest artificial dye-stuffs employed for dyeing textile fabrics were picric acid (prepared from Indigo) and Murexide (from uric acid). Rosolic acid, another early dye-stuff, was discovered by Runge in 1834 and recognised as possessing tinctorial properties; in addition, the same worker observed, on the part of aniline, a number of colour reactions, which indicated this substance as a source of future dye-stuffs.

However, at the time, none of these dye-stuffs and colour reactions could be made the subject of a manufacturing industry, the materials for their preparation being too costly.

Then, in 1856, Perkin found that (impure) aniline

furnished a violet dye-stuff when oxidised. For this industrial preparation or product the conditions were favourable, Hofmann having already discovered benzol in coal tar, and his pupil, Mansfield, having succeeded in recovering it therefrom, on the large scale by distillation. The easy conversion of the nitrated benzol into aniline was also ensured, owing to the already known Béchamp method of amidisation (with iron filings and acetic acid).

All that was lacking in 1856 to utilise these methods for manufacturing the violet oxidation product of aniline on a large scale was the right man; and this man was found in Perkin, who quickly put his product on the market under the name of "Mauve" or "Mauveine". Hence the era of artificial dye-stuffs is rightly dated from Perkin's discovery of Aniline Violet.

The technical success of Mauveine incited numerous attempts to produce other dye-stuffs by the oxidation of aniline, and to discover a better method of preparing Mauveine itself; and these bore fruit in the discovery of a technical method of preparing Fuchsine, by Verguin in 1859.

The scientific and technical investigation of this dye-stuff laid the foundation of the existing important artificial dye-stuff industry. Endeavours were made to discover other oxidising agents for replacing the tin chloride used by Verguin, and in this way the arsenic acid and nitrobenzol process was elaborated. Furthermore, in accordance with the prevailing empirical spirit of research, aniline was submitted to the action of all kinds of reagents, a circumstance which in 1860 led to the discovery of the first artificial blue dye-stuff, Rosaniline Blue, by Girard and De Laire, through heating aniline with Rosaniline. The existence of a secondary action of aniline on Rosaniline had already been deduced from the formation of violet by-products in the Fuchsine

melt. The insolubility of aniline in water was overcome by its conversion into a sulphonic acid by Nicholson in 1862.

The recognition by Hofmann of the true import—a phenylation—of the reaction occurring in the formation of Rosaniline Blue led to his introducing alkyl instead of phenyl into Rosaniline. He heated Rosaniline with ethyl iodide and obtained Iodine Violet (1863), Iodine Green being afterwards (1866) produced by the further action of ethyl iodide.

In this manner was discovered a series of dye-stuffs of hitherto unattainable beauty. Their practical success was great, but this alone did not constitute their importance, the latter being only revealed in the fructifying influence they exerted on the further development of the dye-stuff industry.

The first weighty consequence of the successful alkylation of Rosaniline was the transference of this reaction to aniline itself, a step which led to the discovery of the important dimethylaniline (Ch. Bardy) and the preparation of Methyl Violet (1866) and Methyl Green (1871) therefrom.

The Methyl Violet (or Violet de Paris, so-called from its preparation by Poirrier of Paris) obtained in this manner displaced Hofmann's Iodine Violet, just as Methyl Green took the place of Iodine Green. The first artificial green dye-stuff, Aldehyde Green (1862), had already been driven out by Iodine Green.

We thus see that the first artificial violet and green dye-stuffs were very short-lived. Nevertheless their importance was very considerable, since, on the one hand, they showed the way in which new dye-stuffs could be produced, and on the other the processes of alkylation and phenylation furnished methods of permanent value for the synthetic preparation of dye-stuffs.

A further gain was afforded by the scientific researches pursued with regard to Rosaniline. The investigation of

the conditions attendant on the formation of Rosaniline (Hofmann, Rosenstiehl) revealed for the first time the weighty influence of homology and isomerism. The first practical consequence of this recognition was the separation of Aniline and its homologues, ortho- and para-toluidine. The full importance of the sulphonation of dye-stuffs, first practised by Nicholson, was not revealed until later.

For nearly the entire decade the Rosaniline dye-stuffs monopolised the attention of practical men and the scientific research of dye-stuff chemists. None of the subsequently discovered groups of dye-stuffs had such an influence on the development of the coal-tar colour industry.

A few dye-stuffs of other groups were discovered in connection with Mauveine and Fuchsine. Thus Chrysaniline was isolated from the Fuchsine melt by Nicholson in 1862, and its nitrate, phosphine, played an important part in the dyeing industry as the first yellow tannin dye-stuff. The first Safranine had already been obtained as a by-product of Mauveine (by Perkin in 1863), and also by the oxidation of impure aniline. The nitrobenzol process led Coupier (1867) to the preparation of the first Induline soluble in water, the first spirit Induline having been produced at an earlier date (1863) by Caro and Dale. The scientific investigation of rosolic acid and the production of dye-stuffs therefrom also resulted from the researches on Rosaniline. Finally, the discovery of the first Thiazine, Lauth's Violet (1876), can be attributed to the Aldehyde Green prepared by the aid of thiosulphate.

The same period also witnessed the introduction of Aniline Black, the first of the Azo dye-stuffs, Bismarck Brown (1864), the discovery of two new nitro dye-stuffs, Martius Yellow (1864) and Palatine Orange (1869), and Magdala Red (1868).

Meanwhile the Kékulé benzol theory had been established,

thus opening up a new era in the manufacture of coal-tar dye-stuffs, the former purely empirical search for new dye-stuffs now giving place to well-directed synthesis.

The first example of such a synthesis is afforded by the artificial production of the natural dye-stuff Alizarine, by Graebe and Liebermann in 1869. The great importance of this discovery has already been duly mentioned under Alizarine. It should, however, be stated that the introduction of this article into practice demonstrated the efficiency of two of the most important chemical methods, *viz.*, sulphonation and the sodium fusion process. This rendered practicable the technical production of Resorcline—previously only a laboratory product—and also the manufacture of Fluoreosine (1871) and Eosine (1874).

At this period occurred the accidental discovery of two derivatives of Alizarine, *viz.*, Alizarine Orange (1874) and Alizarine Blue (1877).

Whilst the chief attention of the coal-tar colour industry was still occupied with artificial Alizarine, another class of dye-stuffs, the Azo dye-stuffs, appeared on the market in 1876. The Azo compounds themselves had already been discovered by Griess, and their constitution elucidated by Kékulé; moreover, a few dye-stuffs of this group were known, one of them (Bismarck Brown) being already on the market. It was not until the year in question, however, that the discovery of Chrysoidine by Witt and Caro revealed the eminent technical value of the Griess method for the production of Azo dye-stuffs.

Almost simultaneously, Roussin discovered the Orange dye-stuffs from sulphanilic acid and the naphthols. These were dye-stuffs of high technical importance, and in addition they led to the technical production of sulphanilic acid and the important technology of the naphthols.

There soon arose a series of beautiful yellow to orange-

coloured acid dye-stuffs, which first commenced as successful rivals of the nitro dye-stuffs; and it was initially believed that the Azo group was only capable of furnishing yellows, though this was dispelled by the discovery of Fast Red by Caro in 1877.

In all these products the sulpho group for the first time was seen to play a leading part; and the application of Nicholson's sulphonation method to the other members of the Rosaniline series furnished Acid Fuchsine (1877), Acid Violet, and finally—by the sulphonation of the Malachite Green, first discovered in 1878 (Fischer, Doebner)—the first Acid Green (1878).

One year after the appearance of Fast Red, occurred the epoch-making discovery of the first Scarlet dye, the Hoechst Ponceau (H. Baum), by means of which the Azo dye-stuffs acquired premier place. Moreover, the weighty influence exercised by the position of the sulpho groups on the tinctorial character of the dye-stuffs was perceived for the first time in the divergent behaviour of the salts R and G employed in the preparation of the Ponceaus.

These latter were quickly followed by the first red tetrazo dye-stuff, Biebrich Scarlet (1878), and others; and as afterwards the practice was adopted of using naphthalene derivatives exclusively, in the preparation of such dye-stuffs the first Black Azo dye (Blue Black, 1882, Glaser) was obtained.

The year 1880 witnessed the completion of a long series of researches on Indigo which led Adolf Baeyer to the artificial production of this dye-stuff—the most celebrated of all syntheses of dye-stuffs.

To the same period belongs the discovery of the most important of the nitro dye-stuffs, Naphthol Yellow (Caro, 1879).

The introduction of Phosgene in the eighties (Ad. Kern)

gave a new turn to the synthesis of dye-stuffs. The first of the so-called Phosgene dyes, Crystal Violet (Kern), appeared in 1883; and the application of Phosgene enabled symmetrical and asymmetrical Rosaniline dye-stuffs to be built up in any convenient manner, and finally led to the discovery of Auramine (Caro and Kern, 1884).

An entirely analogous action was exerted by the subsequently introduced formaldehyde (1889), by the aid of which Leonhardt constructed his Pyronines and various Acridine dye-stuffs; it also led, in the triphenylmethane series, to the preparation of New Fuchsine (Hoechst), Formyl Violet (C.) etc.

To the same period also belongs the discovery of Tartrazine (1884), Rhodamine (1887), Azocarmine (1888), the introduction of the nitroso dye-stuffs and Oxazines, and the discovery of the Rosindulines by O. Fischer and Hepp.

Two other discoveries of very wide-reaching practical importance were made during the eighties. The first of these was the production of Congo Red (Boettiger, 1884), the first representative of the group of dye-salts which focussed the attention of the dye-stuff industry for a whole decade.

The second important novelty consisted in the introduction of sulphuric acid, rich in anhydride, for the production of polyoxyanthraquinones and Anthraquinoline dye-stuffs (Bohn, 1888, and R. Schmidt, 1890). By this method the group of the Alizarine dye-stuffs was enriched by a number of valuable blue and green mordant dyes (Alizarinecyanines, Anthracene Blue, Alizarine Viridine, etc.); it also finally led to the discovery of Alizarine Saphirol (Fr. By., 1898), a dye-stuff possessing the still uncommon property of giving, in an acid bath, handsome blue dyeings that are very fast to light.

A third very important acquisition at this period was the introduction of Azo dye-stuffs developed on the fibre, a

method which took its rise in Primuline (Green, 1888), and the patents of Holliday (1880) and Graessler (1881), and attained the apex of its technical development in Nitraniline Red.

The most recent period of the coal-tar colour industry is characterised by two acquisitions of high importance: the introduction of Indigorein (1897) and the Sulphine dyes.

Thanks to the unexampled expenditure of time, money and energy on the part of the Badische Anilin- und Soda-fabrik, the problem of replacing natural Indigo by an artificial product has at length approached solution. At present, synthetic Indigo can be produced by K. Heumann's method at a price enabling it to compete with the natural article. On the other hand, it is also hoped to find, in the highly appreciated group of the Sulphine dyes, products capable of replacing Indigo as well as Logwood and other natural dye-stuffs—so far as cotton dyeing is concerned.

This short review cannot be terminated without mentioning a discovery which, though for the moment devoid of technical interest, is, nevertheless, of high scientific and general importance, *viz.*, the recently effected synthesis of Luteoline by St. von Kostanecki.

It has already been stated that the history of the artificial dye-stuffs may be divided into two periods: the earlier one characterised by the prevalence of an empirical search for new dye-stuffs, whilst the feature of the later period is rational synthesis—a consequence of the Kékulé benzol theory.

An examination of the methods of colour makers at the present time reveals that the existence of a new factor influencing the synthesis of dye-stuffs has come into play, namely, an intimate mutual connection between the production and application of dye-stuffs, between colour manufacture and dyeing. Whereas, in former days, the synthesis of new dye-

stuffs was commenced from a purely chemical standpoint, the endeavour now is to find a dye-stuff that shall meet some practical requirement. The fruit of the aforesaid connection is seen in the successful introduction of Anthracene Brown and Alizarine Black (B. A. S. F.), the preparation of various Alizarine and Anthracene Yellows, etc. The introduction of chrome mordants into the dyeing process, and the constantly increasing need of fast dyes, have also exerted considerable influence on the manufacture of dye-stuffs.

On the other hand, it is only of late that the most important property of dye-stuffs, *viz.*, their tinctorial character and the behaviour of their dyeings, has received its due share of attention by the dye-stuff manufacturer. At the present time all dye-stuff makers make comparative tests of the fastness of their products, rightly recognising that this is the sole means of attaining the ideal of the practical synthesis of dye-stuffs, *viz.*, the complete elucidation of the connection between the constitution of a dye-stuff and its properties.

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Dr. H. Caro, *Ueber die Entwicklung der Theerfarbenindustrie* (Berlin, 1893). This classical work gives a complete history of the development of the artificial dye-stuff industry.

THE NATURAL DYE-STUFFS.

This designation comprises all the dye-stuffs met with in nature. Some of them have also been prepared by artificial means, such as the valuable tinctorial principle of Madder and Indigo. Nevertheless they will also be dealt with in the present section, since the commercial products are of

quite a different nature to the artificial products, and therefore must be considered from a technological standpoint, as well as from the purely scientific side dealing with the contained tinctorial principles.

Before the discovery of the artificial dye-stuffs these natural products were almost the only colouring materials at the disposal of the dyer and cloth printer, a few mineral pigments being used to only a limited extent. Their practical value may be gauged by the fact that some of them are still in use, despite the large number of existing artificial dye-stuffs. The cause of this is to be sought, not, as some are inclined to assume, in the conservative character of the practical dyer, but mainly in the fact that no equal or superior substitutes for them have yet been found. Where, however, this has been the case it has not taken long for the natural dye-stuff to be ousted by its artificial substitute. Thus the artificial Alizarine very soon drove the formerly important and highly appreciated Madder out of the field; the valuable Cochineal has had to give way to the (for many purposes) cheaper Ponceaus; Fustic has been displaced by Galloflavine, Alizarine Yellow, etc.; Santal by Cloth Red, and Archil by a large number of superior artificial dye-stuffs. On the other hand, Indigo, Logwood and Catechu are still indispensable, and have not suffered to any considerable extent by the competition of the in part very good substitutes proposed for them. Furthermore, no really equivalent substitutes have yet been discovered for the less important natural dye-stuffs, Quercitron (wool dyeing) and Buckthorn berries (calico printing).

In the discussion of this question, however, it must not be forgotten that the undiminished consumption of Indigo and Logwood is for the most part due to the increased demand for dye-stuffs of all kinds. At the present time many fabrics and yarns are dyed blue and black, with

artificial dye-stuffs, that were formerly dyed with Indigo and Logwood exclusively.

If we desire to classify the natural dye-stuffs according to their practical importance, it will be necessary to divide them into three groups:—

1. Indigo, Logwood, Catechu.
2. Buckthorn berries, Quercitron.
3. Cochineal, Lac-dye, Redwood, Santal, Fustic, Archil.

Of the remainder, Madder, Woad, Curcuma, Camwood, Indian Yellow and Fustet wood still find restricted local employment.

Naturally in this case the dye-stuffs cannot be divided according to their constitution, as is done with the artificial dye-stuffs. However, in order to afford an insight into their chemical similarities or differences, a brief consideration will now be devoted to the scientific investigations to which these natural dye-stuffs have been subjected, and to their behaviour in dyeing.

The natural dye-stuffs are in part direct in their tinctorial action (Archil, Curcuma, Safflower, Orleans, the purple snail dyes, etc.); two of them (Indigo, Weld) contain the vat-dye Indigotin; whilst all the rest are mordant dye-stuffs (Logwood, Catechu, Lac-dye, Quercitron, Buckthorn berries, Fustic, Woad, Indian Yellow, Cochineal, Madder, Redwood, Santal, etc.); only Catechu and Santal can also be used for dyeing without mordants.

The following dye-stuffs of this group have been scientifically examined and synthetically prepared: Madder (Alizarine), Indigo, Indian Yellow (Euxanthine), and the colouring matter of Woad (Luteoline). The constitution of the tinctorial principles of Quercitron bark, Buckthorn berries, Fustet Wood, and Fustic, is already known, if not with perfect accuracy; these dye-stuffs being now regarded as derivatives of Flavonol. Finally also, the thick veil which

hitherto enveloped the constitution of the dye-stuffs of Logwood and Redwood, has recently been partly drawn aside.

The natural dye-stuffs are partly of animal, and partly of vegetable origin, and may therefore be divided into two classes.

A. DYE-STUFFS OF ANIMAL ORIGIN.

First among the members of this group are the various purple snails, which impart an extremely fast substantive red to violet colour to vegetable fibres, which colour, for the most part, requires an exposure to light for its development. Some of these were used for preparing the renowned Tyrian purple, which was known as far back as the Mosaic period. In the twelfth century the art of purple dyeing was temporarily lost, its place being taken by Kermes, which in turn was afterwards displaced by Cochineal and Lac-dye.

The three last-named dyeing materials contain the same (?) dye-stuff, carminic acid, which was first isolated by Pelletier and Caventou (1818) from Cochineal.

Kermes.—This product, which is no longer in use, consisted of the dried carcasses of female insects of some twenty species of beetles. The most important of these was the *Coccus ilicis*, which inhabits the ilex (*Quercus ilex*), and is most frequently found in the south of France. Kermes was known in very early ages, but was displaced in the sixteenth century by Mexican Cochineal, which is richer in pigmentary matter.

Cochineal.—This dye-stuff consists of the dried bodies of the female cochineal insect, *Coccus cacti*. This insect, the tinctorial properties of which were discovered in Mexico, in 1518, inhabits plants of the nopal tribe, fields of which are planted in Mexico for the cultivation of the beetle. The plants are gathered from time to time, the beetles found on

them being killed by heat in drying chambers, and sorted through sieves.

Two chief commercial qualities of Cochineal are known : (1) the white or silver grey, and (2) the black Cochineal or "Zaccatila".* The latter is the finer grade and is now the one most largely used. Now that the employment of this dye is so restricted, the commoner sorts, such as Granilla, cochineal dust, and waste, are no longer profitable.

Cochineal preparations that formerly played an important part are: "Red Carmine," obtained by precipitating an aqueous decoction of cochineal with acids; "Carmine lake," the alumina compound of the dye-stuff; "Cochineal ammoniacale," produced by treating cochineal with ammonia.

Cochineal is still used to a small extent, for the production of scarlet and crimson in dyeing silk and wool. The old renowned cochineal scarlet (the tin lake of cochineal) is a dye unsurpassed for beauty and fastness by any furnished by other dye-stuffs. At present these scarlets are generally produced with Ponceaus; but when fast scarlet is required, it must always be obtained by means of Cochineal.

Lac-dye, Lac (stick lack).—These are the commercial names applied to the bodies of the lac insect, *Coccus lacca*. The plants inhabited by these insects are found in Bengal, Hindostan, the Coromandel Coast, etc.

Lac is never used alone, but always in association with Cochineal, in order to increase the fastness of the dyeings. It does not behave in quite the same manner as Cochineal; its dye-stuff is far more sparingly soluble, and it is only with tin mordants that it will furnish usable dyeings, alumina mordants giving very disagreeable browns. Hence lac-dye is much inferior to cochineal in value; moreover, it is fre-

* The silver Cochineal consists of the bodies of the female insects, collected before they have laid their eggs, whilst the second kind are the females gathered after the laying and hatching of the eggs.

quently much contaminated with resin, and therefore liable to produce stains in dyeing.

Indian Yellow, Piuri, Purrée.—In India (Monghyr) the urine from cows that have been foddered on mango leaves, furnishes, when heated, a dye-stuff, the magnesia salt of which is employed, under the above names, as an artist's colour in the country of production. The chief constituent of this dye-stuff is euxanthic acid, which has already been mentioned (p. 214).

B. DYE-STUFFS OF VEGETABLE ORIGIN.

Woad (Pastel).—This name is applied to the plant *Isatis tinctoria*, which, thanks to its (very small) content of Indigo Blue, was extensively cultivated for dyeing purposes in Europe, previous to the introduction of Indigo from the Indigoferæ. At the present time this dye-stuff, which is sold in the form of lumps about the size of a man's fist, is very little used, though it forms an inevitable adjunct, as a ferment, to the so-called woad vat in Indigo dyeing.

INDIGO.

Occurrence.—Indigo is found in plants, and, to a very small extent, also in the animal and human organism.

The plants containing this dye-stuff are very numerous, and mostly belong to the Indigoferæ, chief among them being *Indigofera tinctoria* and *I. pseudotinctoria*. The first named yields the largest quantity, the other the best quality, of this product.

The occurrence of Indigo in the animal and human organism is of relatively insignificant importance in comparison with its occurrence in plants. It has been found in perspiration, pus, and especially in urine. This latter oc-

currence may be of value in diagnosis, since a comparatively large proportion of Indigo is found in human urine, especially in cases of tuberculosis, though it is mostly seen in chronic diseases of the intestines. In urine it occurs in the form of potassium indoxylsulphate, and not as Indican, as was formerly believed. Its presence can be detected by treating a few c.c. of the suspected urine with concentrated hydrochloric acid and chloroform, followed by an alkali hypochlorite. When Indigo is present, the chloroform will assume a blue coloration. This reaction is known as Jaffé's Indican test.

Preparation of Indigo.—Since the Indigoferous plants thrive only in tropical countries, it is only in such lands that the preparation of this product can be pursued, *e.g.* : India (Bengal), Java, Guatemala, China, Africa (Egypt and Senegal), etc. For European consumers, only Indian, Javanese, and Guatemala Indigo comes under consideration.

The cultivation of the Indigo plant is carried on in fields of large area, specially adapted for this purpose. The plants are cut at flowering time, which is generally a few months after sowing, since they are found to contain the largest proportion of Indigo when in that condition. The number of cuttings varies according to the climate, but generally averages three in a season.

The cultivating industry is attended with difficulties, and the result, or final yield of Indigo, varies considerably, the proportion of dye-stuff in the plant being affected, to a great extent, by many conditions: soil, climate, etc. The chief factor, however, determining the yield is the quantity of leaves produced by the plant, these being the parts richest in Indigo.

After harvesting, the plants are generally conveyed, with a minimum of delay, to the factories. Here they are treated in the following manner. The bundled plants are first placed

in steeping vats, where they are immersed in water, and left to soak for some time. The object of this operation, which is known as fermenting, is to bring into solution the Indican contained in the plants, and from which the dye-stuff is obtained.

According to Van Lookeren-Campagne, Indican is a compound of Indigo White and dextrose. Formerly it was supposed that a separation of these components was effected by fermentation in the steeping vat; but, according to H. Molisch and Van Lookeren-Campagne, the active agent is an enzyme present in the leaves.

After a short time, almost the whole of the Indigo in the plants has passed into the water, in the form of Indigo White. This process of extraction, however, must not be too prolonged, since excessive "fermenting" spoils the quality of the Indigo; on the other hand, if the fermentation be too short, a portion of the Indican remains unextracted. As soon as it is found, by various signs, such as smell, colour, and taste of the liquid, the blue scum collecting on the surface, etc., that the extraction process has lasted long enough, then the liquid is transferred from the steeping vats to a series of so-called beating vats, standing on a lower level. The liquid now consisting of a solution of Indigo White,* it is now merely a question of converting the same into Indigo Blue by oxidation. Atmospheric oxygen is the agent used, the method adopted being to bring the liquid in the vats into intimate communication with the air, by beating and stirring it up by the aid of sticks, paddles, etc.

In a short time the whole of the Indigo is separated in an insoluble condition, but the beating is still continued for a little while, in order to bring it into a state ensuring rapid and complete deposition. This done, the supernatant clear

* It is not impossible that the Indigo in this solution is in the form of indoxyl, and not Indigo White.

liquid is drawn off, and the Indigo is filtered, after which it is generally boiled, and is finally cut into lumps and dried.

The dyeing is conducted very slowly and carefully in special drying houses, which must be well ventilated and shaded. The more gradual the drying, the finer the structure of the Indigo and the more readily will it be soluble in the dyeing vat. The yield of Indigo obtained in this manner is about $1\frac{1}{2}$ to 2 per cent. of the weight of the plant.

Varieties of Indigo.—As already mentioned, only Bengalese, Javanese and Guatemala Indigo are of any importance for the European market. Each of these three varieties has its special characteristic properties and peculiarities by which it can be recognised; and each is divided into a number of sub-varieties, the quality of which mainly depends on the nature of the soil in which the plants were grown.

It sometimes happens that two adjoining factories turn out products very different in character, and even one and the same factory is not always able to keep to the same standard. Generally, however, the character of Indigo prepared in a given place is uniform. As a rule in Bengal, the chief centre of the industry, the quality of the Indigo decreases progressively as the position of the producing factories is more westward. The best Indigo is obtained from the provinces of Lower Bengal and Behar; poorer grades are furnished by Benares, which lies to the west of those already named; and the poorest of all come from Doab and Oude, which in turn lie to the west of Benares.

To facilitate judging, the grades of Indigo are classified according to the districts and provinces from which they are obtained, and are also in part furnished with marks indicating their origin.

This principle, however, is only carried out in its entirety in the case of Bengal Indigo, of which there are over 300

different marks. Very little Java Indigo is sold by marks, and the custom is not applied at all to Guatemala Indigo.

The commercial world also employs special terms denoting the shape, colour or other peculiarities of the Indigo. Thus, according to the shape, a distinction is drawn between half cubes (lumps of Indigo that have been broken in two, either by accident or design), large lumps (the coarse original cubes) and broken pieces (small fragments, sometimes mere granules).

In point of colour the following terms are used : Fine blue, superfine blue, fine violet, purple violet, fine coppery, inferior coppery, etc. The following grades exhibit special peculiarities : Sandy Indigo contains sandy inclusions ; Spotted Indigo consists of lumps interspersed with small white and blue specks ; Avaried Indigo is the name applied to lumps exhibiting an incrustation resembling mould or efflorescent salts ; Burnt or Parched Indigo is Indigo that has been overdried, and consists of friable lumps that easily crumble into more or less blackish fragments, as well as often containing a white internal incrustation ; Striped Indigo exhibits stripes or bands of different colours ; and Greasy Indigo has a greasy fracture and is friable.

Bengal Indigo is the most important of all. The preparation and sale of this variety are almost completely in English hands. It comes on the market in the form of prismatic lumps, each stamped with a mark and bearing the reticulated impression of the linen cloths on which the cakes were laid to dry.

The best kinds exhibit a purple-blue reflex on the freshly broken surface, the inferior sorts showing up pale blue. Special preference for vat dyeing is accorded to the somewhat harder, reddish-violet kinds.

Java Indigo.—This is manufactured and sold by the Dutch, and is the finest of all Indigos. The ash content

and percentage of extractives are very small. The pieces do not exhibit any trace of reticulated impressions, but a characteristic golden sheen is apparent on the freshly broken surfaces. Each lump is stamped with the word "Java". This Indigo is not always rich in colouring matter, being often designedly adulterated with extraneous substances in order to increase the weight.

Of late a grade of reddish-tinged Java Indigo, containing up to 10 per cent. (and more) of Indigo Red, has been produced by the "warm water process".

Guatemala (American) Indigo.—The grades of this Indigo generally belong to the poorest known, and are termed "sobre saliente". On the other hand, the mark Velores is occasionally equal to the best Bengal.

Guatemala Indigo comes on the market in the form of irregular lumps, some of the surfaces being rounded as though turned in a lathe. Another characteristic of this Indigo is the so-called "green coat," *i.e.*, a fine greenish film occurring in patches on many of the lumps.

Valuing Indigo.—The value of Indigo depends in the main on the nature and quantity of the extraneous matters present in variable proportions in all kinds, since the Indigo Blue (Indigotin) in the pure state is always of the same chemical character and value. The best sorts of Indigo contain 70 to 90 per cent. of Indigotin, medium grades 40 to 50 per cent., and the poorer kinds 20 per cent. or less. The other constituents are Indigo Red, Indigo Brown, Indigo glutin, water (3 to 6 per cent.) and ash, the latter consisting mainly of carbonates of lime and magnesia, in addition to alumina and iron oxide.

Indigo that has not been boiled in the course of manufacture contains in addition a yellow extractive, and is of a more greenish colour.

Indigo is frequently adulterated with such substances as

levigated clay and soil, ashes, powdered slate, brick dust, gum, etc., which are incorporated with the Indigo either during or subsequent to the manufacturing process. Finally, a common form of adulteration is to mix inferior sorts with good ones.

The origin and value of samples of Indigo are generally judged by dealers and dyers according to the physical indications; this is, however, a very difficult task, and one requiring lengthy experience. Moreover, the judgment so obtained is not always correct, and a quantitative chemical examination should always be made.

The main physical criterion is the structure, which should be of a fine paste-like character, not granular. At the same time, the Indigo ought to be firm, though of low specific gravity, and not hard. The finer Indigos are open, *i.e.*, the surfaces of fracture are of a soft, floury character, and covered with a fine film; in contrast to this are the inferior close Indigos.

Low specific gravity is a good sign of quality, though it should be remembered that good sorts of Indigo are often loaded. The purer the Indigo the easier it burns; it should be quite dry and easily broken, of a handsome blue or reddish-blue colour, and brighter on the surface of fracture than externally.

Particulars of the chemical methods for estimating the value of Indigo will be found in the author's work, *Chemical Technology of Textile Fibres*.

History and Uses.—Indigo was first brought to Europe (Holland) from India in the sixteenth century. Its introduction was strongly opposed by the cultivators of Woad, and its use was repeatedly prohibited by law. From the commencement of the last century, however, it has been in general use, and to such an extent that it must be regarded as the most important of all dye-stuffs. It is employed for

vat-dyeing cotton and wool, the blues obtained being faster than those furnished by any other dye-stuff. The so-called "blue print" method is based on the ease with which Indigo can be discharged.

In addition, two preparations of Indigo find employment: the so-called Acid Indigo, a solution of Indigo in fuming sulphuric acid, and Indigocarmine, the sodium salt of Indigo-sulphonic acid. The first of these is used in dyeing wool, the other for silk and wool. Their practical value is, however, low, and they have already, for the most part, been superseded by superior artificial dye-stuffs.

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MADDER.

(Fr., *Garance*; Ger., *Krapp*.)

This product has been employed, from time immemorial, in the so-called "Turkey Red" method of dyeing, and enjoyed a great reputation previous to the introduction of artificial Alizarine in 1869. In the sixties, the production of madder amounted to about 70,000 tons per annum, and the value to £3,000,000 or £3,500,000 sterling; but by the end of the seventies, the consumption had declined to such an extent that the plant was no longer worth cultivating, and now the dye is restricted to a few specialties in wool dyeing.

Madder is the powdered root of the plant *Rubia tinctorum*. Its chief constituent is ruberythric acid, which was first obtained in a crystalline state by Rochleder. This acid is a glucoside, and, under the influence of acids, splits up into Alizarine and a sugar. Alizarine was first obtained in a pure state, from the madder root, by Robiquet and Colin.

Madder also contains Purpurine, Pseudopurpurine (Carbopurpuric acid), Munjistine or carbopurpuroxanthic acid (in Indian madder), xanthine (Kuhlmann), probably a mixture of several yellow dye-stuffs, Chlorogenine (Schunk), or rubichloric acid (Rochleder), a substance which furnishes a green dye-stuff on decomposition ; glucosides, sugar, gum, etc.

To improve the qualitative and quantitative yield of the madder root, it was formerly the practice to treat it with acids, steam, etc., and in this manner numerous "madder preparations" were obtained. Madder extracts were prepared by treating the root with various solvents. These products played an important part in calico printing.

At the present time, as already mentioned, the employment of Madder is merely insignificant, and all that need be stated further is that the inferior grades are known in practice under the name of "Red" (Ger., *Roethe*), a distinction being drawn between roots gathered in the summer and autumn respectively.

History.—Madder was cultivated in the Levant in the earliest times, and its use in dyeing was known to the Egyptians, Persians and Hindoos. From the Orient the root was introduced into Italy, as Lizari or Alizari ; in the middle of the sixteenth century, the Dutch began to cultivate the madder plant. Later on Charles V. introduced it into Alsace, and Colbert into Avignon ; and finally it spread to north Germany. At the time of its greatest popularity it was chiefly grown in the south of France, Alsace, Sicily, Tuscany, Austria-Hungary, Holland, Silesia, Bavaria, Caucasia, East Indies, North and South America, Algeria, etc.

In the Middle Ages, madder was known as Verancia or Varancia (from *vero* = true), from whence its French name, *garance*, is derived. The origin of the German appellation, *krapp*, is doubtful.

Of the madder preparations already referred to, that known

as *fleurs de garance* was the most important (Julian and Roquer, 1851). This product was obtained by steeping the ground madder roots in slightly acidified water, and leaving to ferment for some time, alcohol being recovered from the solution. A less handsome product, but one richer in colouring matter, was prepared by boiling the above preparation with a fairly strong acid; it was called "Garancine," and in a similar manner a product known as "Garanceux" was obtained from old dye-baths. Pinkoffin, or commercial Alizarine, was prepared by the action of superheated steam on Garancine, and was specially adapted for the production of violet dyes.

LOGWOOD.

(Fr., *Bois de Campêche*; Ger., *Blauholz*.)

This highly important dyeing material is the wood of a tree, *Haemotoxylon campecnianum*, which grows wild, especially in Central America, Jamaica, Domingo, Hayti, Cuba, Martinique, etc., and is also cultivated of late years.

The Spaniards were the first to become acquainted with Logwood: after the Gulf of Campeachy, from which it was principally obtained, they named it Palo Campechio, from which comes the name Campeachy wood. It appears to have been introduced into England shortly after the accession of Queen Elizabeth, but, as happened in the case of Indigo, its use was very soon prohibited by law. This notwithstanding, it quickly made headway, especially for silk dyeing, in which it acquired the predominant position it has retained to this day.

Its chief use is for black dyeing on silk and wool, and for blue on this latter fibre (Wood Blue); to a subordinate extent it is also used for black on cotton. In addition it is employed to a smaller extent for the production of mixed

colours (drab, brown, grey, etc.) on cotton, wool and in calico printing. The greatest damage done to the employment of this dye-stuff in cotton dyeing and calico printing, was by Aniline Black and Diamine Black; whilst in wool printing, it has been entirely superseded by Naphthol Black (C.) and similar dye-stuffs. On the other hand, Logwood still plays a leading part in the black dyeing of wool, though even here a number of articles are now dyed by the aid of Naphthol Black (C.), Alizarine Black (B. A. S. F.) and Diamond Black (By.). Nevertheless, despite the excellence of these artificial dye-stuffs, the Logwood Black produced with the aid of iron and copper, as mordants, still remains the best black for wool; and in the black dyeing and printing of silk, Logwood is unrivalled.

The chief kinds of Logwood are: Campeachy, Jamaica, Domingo, Hayti, Yucatan and Honduras wood.

The finest and best sorts are the Campeachy Logwoods, and of these, Laguna Campeachy takes the lead. The less valuable Yucatan, Campeachy-Campeachy and Honduras Campeachy Logwoods are held in good repute for the preparation of Logwood extracts. Nevertheless, a good deal of Laguna wood is extracted, the product being known as "Haematin". Of late, owing to the increased inquiry for, and growing scarcity of, good Logwoods, even the lower qualities have gone up in price and reputation; and latterly, the roots, especially of the Jamaica kinds, have been largely used for extraction.

Of the Domingo Logwoods, Morant and Morant Bay is chief, Fort Liberté wood being also appreciated. Even poorer kinds, however, especially the better qualities of Monte Christo wood (Sabanete), are largely used for wool dyeing.

Of the Hayti woods St. Marc and Artibonite are principally dealt in.

As is the case with Indigo, the market price is not always an accurate expression of the value of a Logwood. For many purposes, *e.g.*, extraction, the cheaper kinds are occasionally more advantageous than the dearer sorts.

Again, the foregoing classification of the Logwoods, according to which the chief place is given to the Campeachy woods, does not altogether apply, good qualities of Fort Liberté wood, for example, being often preferred to some kinds of Campeachy.

With regard to the consumption of Logwood, the following table gives the figures showing the great increase that has taken place in the past three decades :—

Year.	Imports of	
	Campeachy Logwood.	Domingo and Jamaica Logwood.
1868 . .	18,400,000 lb.	17,000,000 lb.
1880 . .	28,100,000 „	26,300,000 „
1893 . .	30,700,000 „	35,600,000 „

The extraction and fermentation of Logwood are fully described in the author's *Chemical Technology of Textile Fibres*.

The name "Indigo substitute" is applied in commerce to a Logwood extract which is blue instead of brown in colour. It is obtained from the ordinary extract by treating with chrome salts and oxidising agents.*

The reduced black (*Noir réduit*) often used in calico printing is prepared in the following manner. Logwood extract is stirred up with a little acetic acid, and then treated with a mixture of potassium bichromate and sulphuric acid. The resulting precipitate is dissolved in sodium bisulphite,

* A usable "Indigo substitute" can be prepared as follows: A mixture of 169 c.c. of Logwood extract, 60 c.c. of water, 2 grms. of sodium chlorate, and 40 c.c. of 6° B. acetic acid is boiled for some time, then cooled, treated with 20 c.c. of green, 16° B. chromium acetate, and slightly warmed again (see also *Leipziger Monatsschr. f. Textilindustrie*, 1891, No. 9).

and when suitably thickened can then be used direct for printing as a steam black.

Chemistry of Logwood Dye.—The colouring principle of Logwood, *viz.*, Haematoxylin, occurs in the form of a glucoside, *i.e.*, in loose combination with a sugar. It is a substance of acid character, and is readily converted by oxidation into the real Logwood dye-stuff, Haemateine. This conversion is effected even by exposing the (purple) ammoniacal solution of haematoxylin to the air. In its turn Haemateine is very sensitive to the action of oxidising agents, and is quickly converted by them into dirty brown-dyeing products, a circumstance that must be borne carefully in mind in the “fermentation” of Logwood. It cannot be reconverted into haematoxylin by reducing agents.

Haemateine is an adjective “dye-stuff,” its own colour being so weak that, without the aid of mordants, it produces merely a light grey on wool. With the mordants in practical use it furnishes the following colours:—

With zinc mordants . . .	Violet
,, alumina mordants . . .	Blue
,, chrome mordants . . .	Blue black
,, iron mordants . . .	Black
,, copper mordants . . .	Greenish-black

On leaving an ethereal solution of haematoxylin treated with a little sulphuric acid to stand for a while there results, not Haemateine, but the isomeric β -Haemateine, which differs from the first named inasmuch as it can be acetylated and can also be reconverted into haematoxylin by reducing agents (sulphurous acid).

Haematoxylin is the only substance that has been investigated scientifically. The alkylation experiments of J. Herzig* showed that it contains five hydroxyl groups.

* *M. f. Ch.*, 15, pp. 143-146.

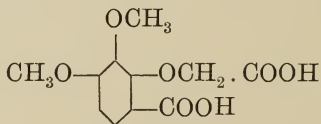
In the first place, a tetramethyl derivative is obtained, which can be converted by acetylation into monacetyltetramethylhaematoxylin, and by energetic alkylation into pentamethylhaematoxylin. Consequently, the hydroxyls of haematoxylin do not all exhibit the same behaviour on alkylation, four of them being more easily alkylated than the fifth. Similar conditions are found to prevail among the xanthenes and flavones, the conclusion therefore being that a certain similarity must exist between the still undetermined constitution of haematoxylin and that of these substances. The same applies also to Brasiline, which will be described later on.

As was found by Herzig, four hydrogen atoms in acetyltetramethylhaematoxylin can be eliminated by oxidation, without the function of the oxygen atoms being interfered with thereby—except for the fifth, which now reacts as phenolhydroxyl, whereas in the unoxidised haematoxylin, it behaved as an alcohol hydroxyl. This proves that haematoxylin is a hydrated substance. Brasiline also behaves quite analogous to haematoxylin in this respect.

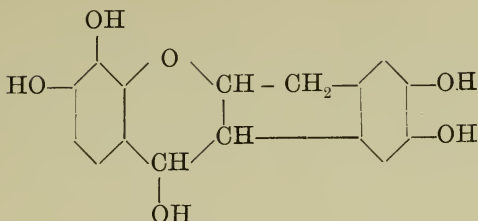
The problem as to the constitution of haematoxylin has latterly approached solution, W. H. Perkin and his colleagues having succeeded, by the oxidation of methylated haematoxylin, in obtaining *m. hemipinic acid* :



and an acid of the composition :—



They therefore believe that the constitution of haematoxylin may be expressed by the formula :—



Of the other chemical properties of these substances, mention may be made of the following: haematoxylin, which was first isolated by Chevreuil and first prepared by Erdmann (by extracting Logwood with ether), corresponds to the formula $C_{10}H_{14}O_6 + 3H_2O$. Its solutions are strongly dextro-rotatory. With bases it furnishes colourless compounds, exhibiting a great tendency to become coloured. When boiled with potash, it gives formic acid; when fused with that alkali, pyrogallol; and when subjected to dry distillation, Resorcine (?) and pyrogallol. In addition to the foregoing ethers, a phthaleine and bromine derivatives of haematoxylin have been prepared.

Haemateine corresponds with the formula $C_{16}H_{12}O_6$; it forms reddish-brown microscopic plates, with a yellowish-green metallic lustre. An isohaemateine has also been prepared.

REDWOOD.

(PERNAMBUCO WOOD, BIRCH REDWOOD, BRAZIL WOOD, SAPAN WOOD, ETC.)

These woods come from trees of various species of *Caesalpinae*, belonging to the genus *Leguminosae*. They are met with in South America, the Antilles, Jamaica, Eastern Asia (Sapan wood), etc., etc. Pernambuco is the finest quality, Costa Rica and Ceylon Sapan being inferior sorts.

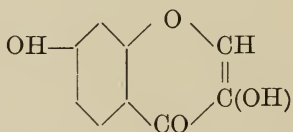
At the present time the Redwoods are only very little used in calico printing (as extract) and in cotton dyeing for

the production of mixed colours. The dye-stuff is mainly fixed with chrome mordants (red brown), partly also with alumina mordants (bluish-red). These dyeings are not very fast, and are merely used on account of their cheapness.

The colouring principle of Redwood behaves quite analogous to that of Logwood. It bears the name "Braziline" ($C_{16}H_{14}O_5$), and, just like haematoxylin, is converted into the true dye-stuff, Brazileine ($C_{16}H_{12}O_5 + H_2O$), by oxidation. An isobrazileine has also been prepared. Herzig* on the one hand, and Schall and Dralle† on the other, have investigated the behaviour of Braziline on alkylation and acetylation. Like haematoxylin it gives a trimethylether, which is converted, by acetylation, into monacetyltrimethylbraziline, and into tetramethylbraziline by energetic alkylation. This proves that Braziline contains at least four hydroxyl groups, and that these do not all behave alike.

As was the case also with haematoxylin, Herzig succeeded in eliminating four of the hydrogen atoms by oxidation, and obtained a product, all the hydroxyls of which can be readily alkylated.

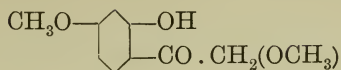
Recently attempts have been made to build up structural formulæ for Braziline. As far back as 1888, Schall and Dralle, by oxidising an alkaline solution of Braziline with atmospheric oxygen, obtained the compound $C_9H_6O_4$, which, according to von Kostanecki and Feuerstein, is a 3. oxypheno- γ -pyronol:



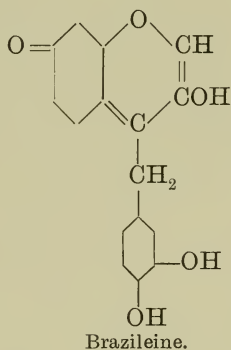
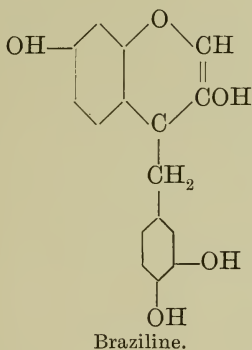
since its dimethyl ether can be easily decomposed by sodium alcoholate into Herzig's fisetoldimethylether,

* *M. f. Ch.*, **14**, pp. 56-58; **15**, pp. 139-146.

† *Berl. Ber.*, **xx.**, p. 3365; **xxi.**, p. 3009; **xxii.**, p. 1547; **xxiii.**, p. 1430.



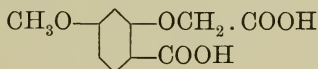
and formic acid. Since, moreover, Herzig has proved the presence of the protocatechuic acid radicle in Braziline, the following constitutional formulæ (von Kostanecki and Feuerstein*) should therefore correspond to Braziline and Brazileine:—



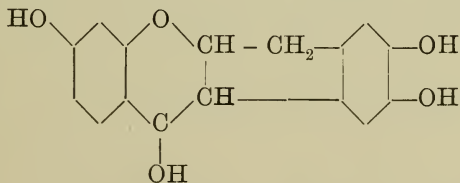
The same formula was simultaneously constructed by Schall; but Perkin and Gilbody chose a different one, since by the oxidation of trimethylbraziline they obtained m. hemipinic acid,



and a methylcarboxylresorcylic acid,



and consequently they ascribed to Braziline the formula:—



* *Berl. Ber.*, 1899, p. 1024.

The empirical formula of Braziline is $C_{16}H_{14}O_5$. It forms amber-yellow crystals, and furnishes Resorcine on dry distillation, or, when fused with potash, Resorcine, pyrocatechuic acid, formic acid and acetic acid; treatment with potassium chlorate and hydrochloric acid gives isotrichlorglyceric acid, and with nitric acid trinitroresorcine.

Chloro and bromo derivatives of Braziline have also been prepared, as well as various ethers.

Brazileine ($C_{16}H_{12}O_5 + H_2O$) forms reddish-brown tables, with a grey metallic lustre, and is prepared from Braziline in precisely the same manner as Haemateine is from haemat-oxylin.

SANTAL (RED SANDERS WOOD).

(CALIATUR, CAMWOOD, BARWOOD.)

These little-used woods are from trees of the *Pterocarpus* and *Baphia* species. Santal or Caliaturo (East Indian) is mostly employed in wool dyeing,³ especially for topping vat blues, though for this purpose it has very largely been superseded by the various Cloth Reds (Oe., By.) and other dye-stuffs.

These dye woods might also be called red woods, though they differ to a fairly considerable degree from the wood of that name already described. In consequence of the low solubility of their tinctorial principles they are unsuitable for making extracts, and are most advantageously employed by fixing them on the fibre by the darkening method.

Barwood fixed with stannic acid was formerly used for producing an imitation Turkey red on cotton. A similar red is still produced from Santal, and is distinguished by its fastness to acids.

Santalol, $C_{15}H_{14}O_5$, was first discovered in Santal by Pelletier, and has been investigated by Meyer, Weidel and

others. It can be prepared in the same way as Haematoxylin. On oxidation it yields oxalic acid, acetic acid and vanillin (?). When treated with hydrochloric or hydriodic acid, methyl chloride or iodide is eliminated, from which the presence of methoxyl groups may be assumed.

Weidel also prepared from Santal wood the colourless Santal, $C_{16}H_{12}O_6 + H_2O$.

QUERCITRON.

The bark of the *Quercus tinctoria* contains an adjective dye-stuff, which gives fairly fast, handsome orange yellow lakes with tin mordants, and greenish-yellow lakes with alumina and chrome mordants. It is chiefly used for calico printing in the condition of an extract,* either alone or associated with tannin or Alizarine dyes, for the production of the most varied shades of colour. Also in the dyeing of wool and cotton it is still used with advantage, mostly as Flavine in wool dyeing.

Quercitron contains a glucoside, quercitrin, which is split up by acids into the true dye-stuff Quercetin and isodulcite.

Of late the researches on the behaviour of quercitron during alkylation, acetylation, in the potash melt, and in its relationship with Fisetin have led to the elaboration of a structural formula, according to which it would seem to be a flavonol derivative (see Flavones).

The empirical formula of quercitron is $C_{21}H_{22}O_{12} + 2H_2O$, that of Quercetin being $C_{15}H_{10}O_7$ (Herzig). The latter body is a crystalline yellow powder, which splits up into proto-catechuic acid and phloroglucine on mere prolonged contact with caustic alkalis.

* This often deposits quercetin after prolonged standing, and should therefore be well stirred up before use.

In North America is manufactured a quercitron preparation known as Flavine, and largely used *per se* in wool dyeing. Its bright yellow tin lake forms the best yellow for wool, and is either used alone or for yellowing Cochineal scarlet.

As Flavine chiefly consists of Quercetin it therefore behaves in a perfectly analogous manner to quercitron, though of greater value as a dye-stuff, its tinctorial power being up to sixteen times greater than that of quercitron. Moreover, its dyeings are far cleaner since it contains no tannin.*

Flavine is prepared by boiling quercitron with alkaline solvents (5 to 7 per cent. of soda crystals or ammonia, calculated on the weight of the bark). The resulting solution of quercitron is treated with hydrochloric or sulphuric acid, to imperfectly neutralise the alkali, and is then boiled, whereupon the quercitron splits up into Quercetin and isodulcite. The yield of pure dry Flavine amounts to 4 to 10 per cent., is therefore very irregular, and depends mainly on the manner in which the decomposition of the quercitron is conducted. The most usual adulterants are ground bark, common salt and Glauber's salt. A good Flavine should not dissolve entirely in boiling water, and the solution should be pale and turbid. An addition of aluminium sulphate should not give any precipitate, but should immediately turn the solution bright yellow.

BUCKTHORN BERRIES.

The dried unripe fruit of certain species of *Rhamnus* furnishes an extract which produces a very handsome and fast yellow tin lake, which is used in calico printing and

* Aqueous solutions of Flavine lose their tinctorial power entirely when stored in open vessels for a few days, a point that should be borne in mind by the dyer.

for which no adequate substitute has yet been discovered among the artificial dye-stuffs. This lake is also sold in paste form, and is used as an albumin dye in calico printing.

Buckthorn berries contain a glucoside, xanthorhamnin, which is split up by acids into the dye-stuff Rhamnetin and isodulcite. Rhamnetin has been identified by Herzig as a monomethylquercetin.

The empirical formula of Rhamnetin is $C_{15}H_9O_6(OCH_3)$. By the action of hydriodic acid one of the methyls is eliminated as methyl iodide, Quercetin being formed. In the potash melt it is decomposed into phloroglucine and pyrocatechuic acid.

WELD.

This dye-stuff consists of the plant *Reseda luteola*, and is used to a very small extent in dyeing wool and silk. Only the yellow tin lake and the greenish-yellow alumina lake, however, come under consideration for this purpose. It behaves in the same manner as quercitron, but is inferior in tinctorial power.

The colouring principle, Luteolin ($C_{15}H_{10}O_6$), has recently been prepared synthetically by von Kostanecki (see Flavones).

FUSTET WOOD.

This is the wood of the Sumach tree, and gives with mordants reddish-yellow dyeings, which, though not very fast, are still used to a small extent for wool. The colouring principle, Fisetin, is allied to Quercetin, which latter, according to Herzig, is a oxyfisetin.

Fisetin, $C_{15}H_{10}O_6$, when fused with potash, is decomposed into Resorcine and protocatechuic acid. It is now regarded as a flavone derivative (see Flavones).

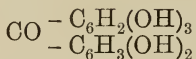
FUSTIC.

(Fr., *Fustel*; Ger., *Gelbholz*.)

Fustic is the wood of the tree *Morus tinctoria*, which grows wild in Cuba, Jamaica, etc., Cuba wood being the best. With tin, alumina and chrome mordants it gives cloudy greenish to brownish-yellow dyeings of low fastness to light, and these are still frequently used for yellow wool in mixtures on account of their cheapness. The former large consumption of Fustic has been considerably diminished by the introduction of Galloflavine, Alizarine Yellow, and other similar artificial dye-stuffs. It is also sold in the form of extract.

Several substances, such as Morin, Maclurin (morinotannic acid) and a tannic acid, have been isolated from Fustic, the dye-stuff being Morin. This latter, $C_{15}H_{10}O_7$, is very similar to the isomeric Quercetin, and is now also regarded as a flavonol derivative (see Flavones). In the pure state it is quite white.

According to Ciamician and Silber, the formula of Maclurin is:—



Its azo compound, prepared from fustic extract, has long been sold under the name Patent Fustine.

CATECHU OR CUTCH.

(Fr., *Cachou*.)

This is the dried sap of certain Acacias, chiefly occurring in India. *Acacia catechu* furnishes the red-brown Bengal catechu; *Areca catechu* the brown Pegu catechu from Bombay. The yellow catechu, also known as Gambier or Cube catechu, is obtained from the leaves of *Uncaria gambir*, Roxb., and *Nauchlea gambir*, Hunter.

In commerce, Catechu is distinguished by marks indicating the origin; these are numerous, the best qualities being: Star B, BB Flag, and Eagle.

Catechu is also frequently called Terra Japonica, which is not quite correct, Japonica being the special quality of Catechu mentioned above as Gambier.

Catechu is an extremely valuable dye-stuff, although limited in its application. It is used only for silk dyeing—chiefly on account of its tannin—in cotton dyeing and calico printing for browns. The colour obtained is red-brown or grey-brown, according as chrome or iron mordants are used; neither is handsome or bright, but both are extremely fast.

There are two chief constituents of Catechu: Catechin and catechutannic acid, the former being the dye-stuff. Catechin is colourless, and is converted, on oxidation, into a brown substance, japonic acid.

Gambier is said to contain three different Catechins.

Catechin, $C_{21}H_{20}O_9 + 5H_2O$, or $C_{18}H_{18}O_8$, gives phloroglucine and protocatechuic acid when fused with potash; and on dry distillation furnishes pyrocatechin, acetic acid and phenol.

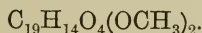
A diacetyl- and a dibenzoylcatechin have also been prepared.

CURCUMA OR TURMERIC

is a substantive dye-stuff composed of the root nodules of *Curcuma tinctoria*. It is still used to a small extent in silk dyeing.

The colouring principle, Curcumin, forms yellow prisms with a blue reflex. It furnishes vanillin when oxidised with potassium permanganate.

According to Ciamician and Silber its formula is:—



ARCHIL (ORCHIL, ORSEILLE, PERSIO).

It has long been known that certain lichens of the *Roccella* and *Lecanora* species (Canary Islands, East Indies, South and Central America, etc.), when exposed to the air in presence of an alkali, furnish bluish-red dye-stuffs which act as substantive dyes on wool and silk. Formerly the above plants were treated with stale urine (ammonium carbonate) for the preparation of the dye-stuff, lime being added from time to time, and the whole left for several weeks, with occasional stirring. At present the practice is to stir up the lichens in water, and pour the whole into a sieve, which retains the woody portions and allows the tinctorial parts to pass through, either as powder or in solution. The resulting liquid is then treated with ammonia and is warmed for some time in open vessels, the deposited dye-stuff being sold in the form of paste.

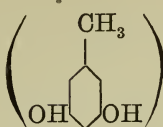
Persio or Cudbear is an orchil prepared from *Lecanora* lichens, chiefly in Scotland.

Litmus, the well-known indicator, is also obtained from the same plants by a somewhat longer treatment with alkalis, mainly in Holland. Gypsum or chalk is generally added.

Previous to the introduction of artificial dye-stuffs, Archil played a very great part in the dyeing of wool and silk. True, the colouring principle is very fugitive, but it equalises well, and can be used either in a neutral, acid or alkaline bath.

At present its use is small in these branches, having been driven out by Methyl Violet, the Acid Violets and various red Azo dye-stuffs (Azofuchsine, Azoorseille, Chromotrope, etc.).

The chief constituent is Orcein ($C_7H_7NO_3$), obtained by the oxidation of Orcin,



by atmospheric oxygen in presence of ammonia.

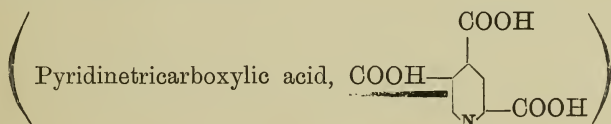
Dye-stuffs of this kind have been artificially prepared by Zulkowski in collaboration with Peters.

Litmus contains several colouring matters.

Safflower (saffron), obtained from the dried flowers of *Carthamus tinctorius*, was at one time chiefly used for rose colour on cotton. The dyeings are very fugitive, but, being obtainable without the aid of mordants, were in great favour. The chief constituent is Carthamin ($\text{C}_{14}\text{H}_{16}\text{O}_7$) (?), a yellow colouring matter being also present.

Orleans is obtained from the flesh of the fruit surrounding the seeds of *Bixa orellana*. It gives salmon red to orange dyeings, which are also substantive for cotton. It is no longer in use. The chief constituent is Bixin ($\text{C}_{28}\text{H}_{34}\text{O}_5$).

Barberry root, from *Berberis vulgaris*, is still sometimes used for dyeing leather yellow and for silk. It contains Berberine ($\text{C}_{20}\text{H}_{17}\text{NO}_4 + 4\frac{1}{2} \text{ aq.}$), which gives quinoline when fused with potash, and on oxidation with nitric acid furnishes berberonic acid,



It is therefore an isoquinoline derivative. According to W. H. Perkin,* it is allied to papaverine, hydrastine and nicotine.

Chika, Caraguru are the names given to a red dye-stuff from the leaves of the chika trumpet tree. The dye-stuff is extracted by the Indians of the Orinoco, who use it for painting their bodies.

* *Journ. Chem. Soc.*, i., 991, 1106; *Berl. Ber.*, Ref., 1891, p. 157.

Böhme's Dye-stuffs.—Theodor Böhme of Dresden has put on the market certain products (Carmine dyes) which are prepared by mixing extracts with mordants in well-defined proportions. Some of them also contain tannin dye-stuffs. They are intended for dyeing cotton direct, those containing tannin dyes requiring, however, to be used on tanned cotton. The composition of the chief of these products is as follows (the names indicate the colour produced):—

Leather Yellow and Blonde contain Fustic extract and a chrome mordant.

New Gold contains quercitron extract and a chrome mordant.

Silver Grey contains extracts of Logwood and Redwood, together with a chrome and iron mordant.

Smoke Blue contains Logwood extract and a chrome mordant.

Copper contains Catechu, Safranine, and a copper salt.

Fast Vat Blue R contains Logwood extract, Methylene Blue and a chrome mordant.

MINERAL COLOURS.

The substances belonging to this group are principally used for artists' colours and paints. Consequently they will be only briefly described in so far as they have any interest for the textile industry.

Their use is almost entirely confined to calico printing, either applied as finished colours thickened with albumin, or else developed on the fibre. They are therefore albumin dyes or developing dyes.

Of the first-named kind are Ultramarine, Chrome Yellow, Orange Chrome, Vermilion, Chrome Green, etc. Except Ultramarine, all these are almost exclusively used as so-called discharge dyes in blue printing, being applied in

admixture with an alkali chromate and albumin to a fabric dyed with Indigo. The fabric is then entered in an acid bath, whereupon the Indigo is destroyed at the printed parts by the liberated chromic acid, leaving the mineral pigment unchanged. In this manner coloured designs are obtained on a vat blue ground.

To the developing dyes belong Manganese Bistre and Iron Chamois, which are the most important mineral pigments in the textile industry.

Manganese Bistre.—This, the principal mineral colour used for textile purposes, consists of manganese peroxide, and is prepared in the following manner. The cotton fabric to be dyed is first impregnated with a solution of a manganese salt (sulphate, protochloride, acetate) and dried. It is then run through soda lye, which precipitates manganese hydroxide on the fibre; and the colour is finally developed by oxidation (with bleaching powder, potassium chromate, etc.) in a third bath.

Thanks to its fastness and the ease with which it can be discharged by reducing agents (tin salt, sulphurous acid, etc.), Manganese Bistre is largely used; and the last-named property has led to its employment for the dyeing of wool (travelling rugs) to imitate skins. The colour in this case is produced by the aid of potassium permanganate, which salt is readily decomposed into manganese peroxide when brought into contact with organic matter.

Iron Chamois.—For the production of this dye, the cotton fabric is impregnated with a solution of ferrous sulphate, on one or both sides (by padding), and then passed through a weak lye. This throws ferrous hydroxide down on the fibre, and the goods are afterwards entered in an oxidising bath of bleaching powder. Consequently the dye consists of ferric oxide. It can be discharged by means of organic (tartaric, citric) acids.

Ochres are chiefly used as coloured dressings for cotton fabrics.

Ultramarine.—This pigment, which is prepared by heating a mixture of alumina, silica, soda, sulphur and carbon, is met with in commerce in a variety of shades from bluish-green to blue and violet, and is used as an albumin dye in calico printing and as “blue” in dressing cottons. Care must be taken in employing it, since it is easily destroyed by acids.

Chrome Yellow and Orange Chrome.—These are chromates of lead, the first being the neutral, the second the basic chromate.

They are sold in the form of paste and are mostly used as discharge colours in blue printing. Sometimes also they are produced on the fibre in calico printing, the pattern being printed with a lead salt and the goods passed through ammonia (formation of the insoluble hydroxide), the operation concluding with a treatment with potassium chromate. This process gives chrome yellow, which can be converted into orange chrome by treating in boiling lime water.

The resulting colours have the drawback of being blackened by sulphuretted hydrogen.

Vermilion is only employed as a discharge colour in blue printing; it is dear and not very fast. Various insoluble red Azo dye-stuffs are used instead.

Chrome Green or *Guignet Green* is produced by fusing boric acid and potassium bichromate, and extracting the melt with water, which converts the chromium borate, first formed, into chromium hydroxide. The product is used exclusively as an albumin dye, mostly in blue printing.

A mixture of Chrome Yellow and Paris Blue is frequently sold as Guignet Green. The real article is frequently termed Permanent Green (in chromo-lithography, bank-note printing, etc., but not in calico printing).

Berlin Blue (Turnbull's Blue).—This beautiful pigment, which was discovered by Diesbach in 1710, was formerly very important for the textile industry, and was used for printing as well as dyeing silk, wool and cotton. It survived longest in cotton dyeing, under the name Potash Blue.

On animal fibres and in calico printing, this blue was produced on the fibre by decomposing an acid solution of potassium ferrocyanide. Thus if wool be entered in a solution of this salt and a little sulphuric acid, and gradually heated to 100° C., it assumes a greenish-blue coloration, handsomer and purer blues being obtained by adding a little tin salt. For the most part, however, Potash Blue was produced by the aid of Logwood. In dyeing cotton, an iron chamois was first produced on the fibre, the blue colour being then developed by treating the fabric with an acidified solution of potassium ferrocyanide.

Berlin Blue is still used in cotton dyeing, in the production of mixed colours in calico printing (adding ferrocyanide to the printing colour), and as a paste colour in dressings.

For other purposes it is sold in the finished state, under various names: Paris Blue, Prussian Blue, Chinese Blue, etc. These colours, being prepared in various ways, do not always have the same composition. The methods employed are: (1) From potassium ferrocyanide and ferric salts; (2) From potassium ferrocyanide and ferrous salts, the resulting ferrous compound being oxidised with potassium chlorate and hydrochloric acid (Paris Blue); (3) From potassium ferri-cyanide and ferrous salts.

Berlin Blue corresponds to the formula $\text{Fe}_7\text{Cy}_{18}$, and may be regarded as a combination of ferrous cyanide and ferric cyanide, $3\text{FeCy}_2 + 2\text{Fe}_2\text{Cy}_6$, or as the ferric salt of hydroferrocyanic acid (H_4FeCy_6), i.e., $(\text{Fe}_2)_2 \cdot (\text{FeCy}_6)_3$. When suffused with caustic potash, it is decomposed into potassium ferrocyanide and ferric hydroxide.

Bibliography.

Reynolds (Abst.), *Berl. Ber.*, 1887, p. 552 c.

For *whitening cloth*, use is still made, to a small extent, of various salts of the alkaline earths: barium sulphate, calcium carbonate, etc. For this purpose the cloth is treated in water holding the corresponding salts in suspension, or is preferably impregnated with a soluble salt (*e.g.*, barium chloride), and afterwards treated with a precipitant (Glauber's salt).

Gold Purple.—The production of gold purple on the cotton fibre has been attempted by Odernheimer (Lehne's *Färber Ztg.*, 1891-92, pp. 205, 375; 1893-94, pp. 4, 207), a gold salt being printed on the fabric in conjunction with a reducing agent (hydroquinone, oxalic acid, etc.). This gives a grey, the shade of which varies according to the reducing agent employed. On then subjecting the printed surface to the pressure of a hot roller (100-110° C.) a handsome red colour, with metallic reflex, is obtained. If the pressure be continued, lustrous metallic gold is produced.

Molybdenum Blue.—This pigment, which consists of oxides of molybdenum, has long been produced experimentally on silk and cotton fabrics, having first been proposed for this purpose by Keller, in 1851. The fabric is impregnated with a soluble phosphate and sodium molybdate, after which it is dried and passed through an acid bath. The yellow colour thus produced is converted into blue by treating with a solution of tin salt.

For dyeing cotton, it would be better to impregnate with a solution of sodium silicate and molybdate, then, after dyeing, enter in a solution of a phosphate, and finally treat with tin salt (Ger. Pat., 69,410, 20th April, 1892).

Uranium Yellow (Ger. Pat., 72,523).—Odernheimer also produced a yellow dye by impregnating the fabric with

uranium nitrate solution, and developing the colour by means of a hot plate applied to the dried stuff. According to the same patent, chromium salts may also be used for producing dyes in presence of reducing agents, green being obtained at lower, and brown at higher, temperatures.

Finally, *Bronze Colours* (Lehne's *Färber Ztg.*, 1892-93, p. 371) are also employed for printing fabrics.

The other mineral pigments, *e.g.*, the bright yellow zinc chromate, barium chromate, Schweinfurt Green (copper arsenite and acetate), Victoria Green (zinc chromate and Chrome Green), Smalt (potassium-cobalt silicate), Thénard's Blue (calcining alumina moistened with cobalt nitrate), Rinmann's Green (salts of zinc and cobalt), etc., are devoid of interest for the textile industry.

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